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Removal of Nitrate from Contaminated Water Supplies for Public Use

Boyle Engineering Corp.
Bakersfield, CA

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REMOVAL OF NITRATE FROM CONTAMINATED WATER SUPPLIES FOR PUBLIC USE

FINAL REPORT

by

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Grant No. R-805900-01-02-03

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16. ABSTRACT

Three treatment processes were evaluated for removing nitrate from public water supplies: Reverse osmosis (RO), ion exchange, and a combination of the two. Both laboratory and field equipment were used to establish design criteria and operating experience useful for designing full-scale plants of approximately 3,800 m^3/day (1-mgd) capacity.

The studies were conducted under EPA grant R 805900-1 awarded to the McFarland Mutual Water Co. (McMWCo) of McFarland, California.

The study is concerned with both engineering and scientific aspects.

The most significant outcome of this work are the findings that:

1. the ion exchange process is generally more suitable as a well site treatment for nitrate removal than RO or a combination of the two. Ion excahnge requires lower first and annual operating costs, greater reliability, less energy, requires no additional well site storage, has higher water recovery, produces a more concentrated waste brine, and requires fewer atuomatic and electrical controls.

2. ion exchange resins with altered chemical structure were formulated for selective removal of nitrate from common groundwaters containing sulfate ions. Projected use of nitrate-to-sulfate selective (NSS) resins in ion exchange plants has potential to reduce operating costs by increasing the efficiency of the process through reduced wastewater, reduced brine requirements, and waste brine disposal costs. These operating cost savings can be estimated to exceed the equipment costs of the plant over a 20-year period.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

The pollution of our nation's groundwater has been called the environmental problem of the 1980s. When polluted groundwater serves as a source of public drinking water, pollutants must be removed to levels below standards regulated by the Safe Drinking Water Act (Public Law 93-523). Nitrate is one of the pollutants frequently found in groundwater used for drinking water supplies and is the cause of serious and occasionally fatal poisonings in infants. This report summarizes studies being conducted in behalf of small communities on processes for removal of nitrate from groundwater supplies.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This research program has the objective to evaluate the general applicability of three treatment processes for removal of nitrate from public water supplies. The processes are reverse osmosis (R.O.), ion exchange, and the combination of R.O. followed by ion exchange. The evaluation consists of using laboratory size and field-test equipment to establish design criteria and operating experience useful for designing a full-scale plant of approximately 1-million gallon per day (mgd) capacity.

An experimental program was conducted using both laboratory size and pilot scale equipment. The program was conducted by the McFarland Mutual Water Co. (McMWCo) at Well 3 in McFarland, California. Ion exchange column tests were conducted with five strong-base anion exchange resins on nitrate-laden waters of various anion compositions. From this work, estimates of product water quality and the bed volume capacity for feedwater of any composition can be made. Also, a working hypothesis was developed from an analysis of the data about how the chemical structure of resins can be practically altered to obtain nitrate selectivity. As a result, a series of resins were synthesized to study the effect of molecular structure on nitrate selectivity. Two of the resins showed selectivity of nitrate in preference to sulfate ion. Others in the series showed enhanced sulfate selectivity.

A 20-inch-diameter pilot anion exchange column was designed and operated for over one year at Well 3. The column contained 4.36 cubic feet of resin. Data from this column operation is used to verify estimates of pilot column performance and to project the cost for equipment and regenerant for a well site installation to treat up to 1 mgd.

An R.O. system having a production capacity of 20,000 gallons per day (gpd) was operated for over 1,000 hours until excessive nitrate passage was obtained.

This is the final report under EPA Grant R-805900-01, 02, and 03 to the McMWCo of McFarland, California, and covers work from June 5, 1978, to June 4, 1981.

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LIST OF ABBREVIATIONS AND SYMBOLS

α^{N}_{Cl} -- Separation factor indicating relative preference of resin for nitrate over chloride.

α^{S}_{N} -- Separation factor indicating preference of resin for sulfate over nitrate.

A-F -- Volume of water, acre-foot.

APHA -- American Public Health Association.

BV -- Bed volume. Relative volume of water compared to volume of ion exchange bed.

BV(N) -- The number of bed volumes of water treated to reach nitrate breakthrough.

BV(N)' -- Bed volumes of water which can be treated until nitrate breakthrough is reached using an incompletely regenerated resin.

C -- Sum of anion equivalents in solution.

$\overline{C}$ -- Exchange capacity of resin, usually expressed in ionic equivalents per liter of resin.

ca -- "circa" meaning approximately.

$\overline{Cl}$ -- Chloride ions in resin phase.

cfm -- Flow rate, cubic feet per minute.

EPA -- Environmental Protection Agency.

eq -- Equivalent.

f -- Fraction of ion exchange bed.

gpm -- Flow rate, gallons per minute.

ID -- Inside diameter of pipe.

K_C^N -- Selectivity coefficient indicating selectivity of resin for nitrate relative to chloride.

K_{Cl}^N -- Selectivity coefficient indicating selectivity of resin for nitrate relative to chloride.

K_N^S -- Selectivity coefficient indicating selectivity of resin for sulfate relative to nitrate.

MCL -- Maximum contaminant level set by Safe Drinking Water Act.

McMWCo -- McFarland Mutual Water Co.

meq -- Milliequivalent.

mgd -- Flow rate, million gallons per day.

mg/l -- Concentration of substance in water, milligrams of substance per liter of water.

ml -- Milliliter.

NCS -- Nitrate-to-chloride selectivity index.

$\overline{NO_3}$ -- Nitrate ions in resin phase.

NSS -- Nitrate-to-sulfate selectivity index.

ppm -- Concentration of a substance in water, parts by weight of substance per million parts by weight of water.

PVC -- Polyvinyl chloride.

R.O. -- Reverse osmosis.

$\overline{SO_4}$ -- Sulfate ions in resin phase.

TDS -- Total quantity of dissolved substance in water. Commonly used to refer to amount of inorganic salts dissolved in water.

X_N -- Equivalent fraction of nitrate ions in solution.

X'_N -- Equivalent fraction of nitrate in regenerant.

$\overline{X_N}$ -- Equivalent fraction of nitrate ion on resin.

$\overline{X'_N}$ -- Equivalent fraction of nitrate ion in nonsulfate portions of resin.

X_s -- Equivalent fraction of sulfate ion in solution.

X'_s -- Equivalent fraction of sulfate in regenerant.

$\overline{X_s}$ -- Equivalent fraction of sulfate ion on resin.

ION EXCHANGE CONVERSION TABLES

VOLUME

	Cu Ft	Gal (U.S.)	Gal (Imp.)	Liters	Cu Meters
1 cu ft	1	7.48	6.23	28.3	0.0283
1 gal (U.S.)	0.134	1	0.833	3.785	0.003785
1 gal (Imp.)	0.160	1.2	1	4.53	0.00453
1 liter	0.0353	0.264	0.220	1	0.001
1 cu meter	35.3	264	220	1,000	1

MASS

	Pounds	Grams	Kilograms	Grains	Kilograins
1 lb	1	453.6	0.4536	7,000	7
1 gram	0.0022	1	0.001	15.43	0.01543
1 kilogram	2.2	1,000	1	15,430	15.43
1 grain	0.000143	0.065	0.000065	1	0.001
1 kilograin	0.143	65	0.065	1,000	1

DENSITY

	Lb/ Cu Ft	Grams/ Liter	Lb/Gal (U.S.)	Lb/Gal (Imp.)
1 lb/cu ft	1	16	0.134	0.160
1 gram/l	0.0624	1	0.00834	0.010
1 lb/gal (U.S.)	7.48	120	1	1.2
1 lb/gal (Imp.)	6.24	100	0.834	1

FLOW RATE*

	BV/ Min	Gal (U.S.)/ Cu Ft/Min	Gal (Imp.)/ Cu Ft/Min	Lb H_2O/ Cu Ft/Min
1 BV/min	1	7.48	6.24	62.4
1 gal (U.S.)/cu ft/min	0.134	1	0.833	8.33
1 gal (Imp.)/cu ft/min	0.161	1.20	1	10
1 lb H_2O cu ft/min	0.016	0.12	0.10	1

*To convert flow rate per volume to flow rate per unit area, multiply flow rate per unit volume by resin volume, and divide by cross-sectional area.

WATER CONVERSION TABLE*

1 cubic foot . . . . 7.48 gallons . . . . 62.4 pounds of water

1 acre-foot . . . . .43,560 cubic feet . . . . 325,900 gallons

An acre-foot covers 1 acre of land 1 foot deep

1 cubic foot per second (cfs) . . . . .445.8 gallons per minute

1 cfs . . . . 646,320 gallons per day

For 24 hours . . . . 1.983 acre-feet

For 30 days . . . . .59.5 acre-feet

For 1 year . . . . 724 acre-feet

1 million gallons . . . . 3.07 acre-feet

1 million gallons per day (mgd) . . . . 1,120 acre-feet per year

1,000 gallons per minute (gpm) . . . . 2.23 cfs

1,000 gpm . . . . 4.42 acre-feet per day

At 10 cents per 1,000 gallons . . . . $32.59 per acre-foot

*Approximate values.

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Mr. Ernest Kartinen, the program manager of this project for Boyle Engineering Corporation.

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SECTION 1

INTRODUCTION

SCOPE OF REPORT

The purpose of this work is to evaluate objectively the general applicability of three treatment processes for removal of nitrate from public water supplies. The processes are reverse osmosis (R.O.), ion exchange, and the combination of R.O. followed by ion exchange. Both laboratory-size and field-test equipment were used to establish design criteria and operating experience useful for designing full-scale plants of approximately 1-mgd* capacity.

The conclusions and recommendations which follow are based on studies conducted under this grant awarded to the McMWCo of McFarland, California. This small community in the heart of the intensive agricultural/industrial area of the San Joaquin Valley in central California is faced with declining water quality and increased demand on their groundwater supply. This problem is typical of many communities not only in the United States but throughout the world. If the development of new water sources from surface supplies or deep aquifers or use of centralized treatment is economically unfeasible, well site treatment for contaminant removal is an alternative that needs to be considered. This report concerns the latter alternative.

Small community water systems have been designed on the basis of supply to the systems through any number of separate wells within the area being served. Loss of any well because of contamination in an in-place system can mean expensive modifications to the entire distribution system. This study concerns those processes which can be applied to a well site situation resulting in improved water quality without constructing new or modifying old wells or altering the distribution system.

Well site treatment for nitrate removal is not considered to be standard practice by professionals in the water treatment field. Only a few such installations can be sited throughout the world, and no detailed operating data or costs have been published. Although ion exchange and R.O. are familiar and widely used processes in industrial water treatment, their application for removal of specific contaminants from community water supplies is new and requires the traditional demonstration project to advance widespread use of these processes. This study provides information and data to aid the planning of a demonstration project.

---

*List of Abbreviations and Symbols is on pages xiv, xv, and xvi, and Conversion Tables are on pages xvii and xviii.

The study reported herein concerned both engineering and scientific aspects. The engineering aspects deal with design parameters, conceptual designs, operation, and process reliability. This data and information were derived from actual hands-on experience by the principal investigator. The scientific aspects deal with ion exchange theory of resin selectivity and testing of new resins which show nitrate selectivity in presence of sulfate and other common anions. It is believed this work has resulted in a major breakthrough in development of nitrate-selective resins which have potential to lower costs of nitrate removal for many communities. The method used to derive the nitrate-selective resins is novel and has general applicability to deriving resins selective for other inorganic contaminants.

An interim report (Reference 1) was prepared under this grant program before all work was completed and covered only work on the ion exchange process to April 1, 1980. This report could not be adequately prepared without several references to the interim report or without repeating some of its information.

Unfortunately, both reports need be studied to obtain a complete picture of the work which was accomplished. It is, however, an objective of this report to be as complete as possible.

Portions of the interim report are included in the Appendix for convenient referral.

The work reported herein was done under EPA Grant R-805900-01-02-03 to McMWCo of McFarland, California. All work was done at Well 3 in McFarland. The results, however, are generally applicable to other communities faced with nitrate problems.

SECTION 2

CONCLUSIONS

GENERAL CONCLUSIONS

1. The ion exchange process is generally more suitable as a well site treatment for nitrate removal than R.O. or a combination of the two. Ion exchange requires lower first and annual operating costs, has greater reliability, uses less energy, requires no additional well site storage, has higher water recovery, produces a more concentrated waste brine, and requires fewer automatic and electrical controls. It can be operated on demand as required by distribution system needs. Such on-off operation is severely detrimental to an R.O. system which operates best on a continuous basis, hence, requires additional storage and repressurization. Brine disposal is a cost common to both processes.

2. Ion exchange resins with altered chemical structure were formulated for selective removal of nitrate from common groundwaters containing sulfate and other common anions. Use of nitrate-to-sulfate selective (NSS) resins in ion exchange plants improves product water quality and has potential to reduce operating costs by increasing the efficiency of the process through reduced wastewater, reduced brine requirements, and waste brine disposal costs. These operating cost savings can be estimated to exceed the equipment costs of the plant over a 20-year period.

The NSS resins require further testing before practical applications can be made. These resins are presently not commercially available, but small quantities were made for this program by a resin manufacturer using existing processes and economically available intermediates.

The NSS resins are examples of structurally induced electroselectivity reversal, a concept which may find applications in removal of other contaminants.

ENGINEERING ASPECTS

1. Design parameters for application of a conventional single-bed ion exchange process with downflow regeneration for

removal of nitrate from well waters were developed and tested using laboratory columns and a 20-inch-diameter pilot column. The process is depicted in Figure 1 for a well water of moderate nitrate and sulfate levels. Pilot column tests were conducted using a Type I strong-base anion exchange resin (Duolite A-101D) at Well 3 in McFarland, California. Well 3 is high in nitrate (ca 90 ppm) and sulfate (ca 320 ppm), making it a useful research well. Modifications were made to a conventional automatic water softener to convert it to the 20-inch anion exchanger pilot column.

2. The study indicates that automatic ion exchange equipment, which is commonly used by the water softening industry, can be adapted for nitrate removal. The equipment can be installed at a well site for direct treatment of well water and operated on demand without storage.

3. The selected resin was effective for nitrate removal for flow rates over 45 gpm per square foot of bed area (2.75 BV per minute). This was the upper limit of the test equipment used. These high flow rates bring the cost of capital equipment and resin quantities to low practical levels.

4. It was found that it is more economical to operate the ion exchange column in a partial regeneration rather than complete regeneration mode when sulfate is present in raw water. This arises from the ability of the resin to concentrate nitrate near the downstream end of the column from which it is easily removed. Salt requirements for McFarland wells range between 2.5 and 5 pounds of sodium chloride per cubic foot of resin. In comparison, complete regeneration would require 18 to 20 pounds per cubic foot. The extended bed life and lower nitrate leakage does not justify the added salt costs. Partial regeneration also produces a water less corrosive than high chloride water produced by complete regeneration.

5. Capital equipment costs of an ion exchange system for treating one-half of a 1-mgd production well are estimated to be less than $100,000 installed. This estimate is based on moderate nitrate levels of less than 60 ppm in well water and sulfate levels less than 200 ppm and blending (50/50) of treated water with raw water to produce a water less than 45-ppm nitrate (see Figure 1). Alternative usage of the same equipment would allow full treatment of the well production rate over 80 percent of the time.

The corresponding equipment cost estimate for a system to treat all water from a 1-mgd production well is less than $160,000.

The total water cost including amortized capital and operating costs are estimated to be 17.3 cents per 1,000 gallons (4.6 cents per cubic meter or 56.38 dollars per A-F) of treated

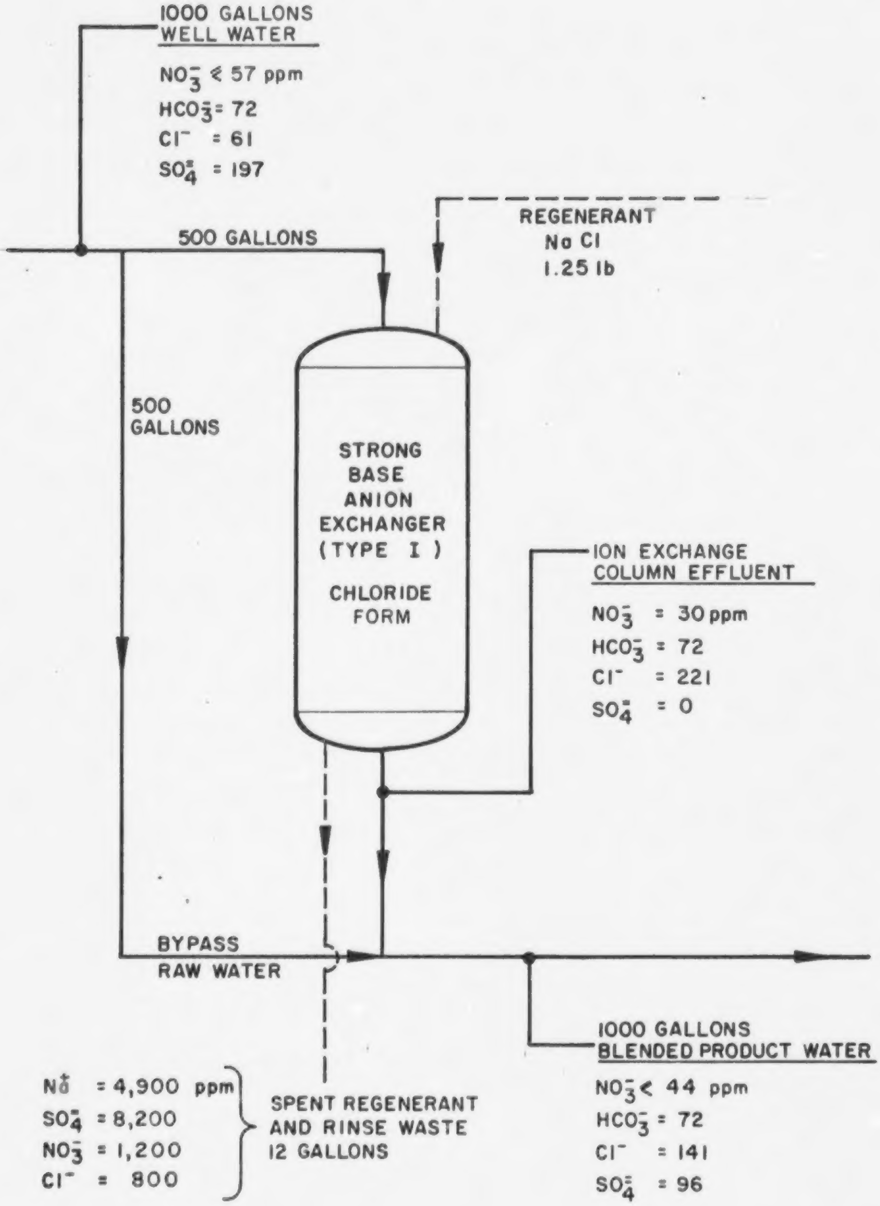

1000 GALLONS
WELL WATER
$NO_3^- \leq 57$ ppm
$HCO_3^- = 72$
$Cl^- = 61$
$SO_4^= = 197$
500 GALLONS
REGENERANT
Na Cl
1.25 lb
500
GALLONS
STRONG
BASE
ANION
EXCHANGER
(TYPE I)
CHLORIDE
FORM
ION EXCHANGE
COLUMN EFFLUENT
$NO_3^- = 30$ ppm
$HCO_3^- = 72$
$Cl^- = 221$
$SO_4^= = 0$
BYPASS
RAW WATER
1000 GALLONS
BLENDED PRODUCT WATER
$NO_3^- < 44$ ppm
$HCO_3^- = 72$
$Cl^- = 141$
$SO_4^= = 96$
$Na^+ = 4,900$ ppm
$SO_4^= = 8,200$
$NO_3^- = 1,200$
$Cl^- = 800$
SPENT REGENERANT
AND RINSE WASTE
12 GALLONS

FIGURE I CONVENTIONAL SINGLE BED ION EXCHANGE PROCESS

water. This is based on raw water nitrate levels of 60 ppm and sulfate levels of 200 ppm and treated water nitrate levels of 30 ppm with all sulfate removed. These costs do not include brine disposal costs which are variable and community dependent. Brine disposal costs can be proportional to regeneration chemical costs if disposed to local landfills and could increase the above unit quantity costs by 30 to 50 percent.

Regenerant costs alone over a 20-year plant life can be more than double the first equipment costs of the plant.

6. Because of the significance of regenerant costs, a method is presented to estimate the sodium chloride requirements for regenerating the resin used in nitrate removal from waters of various composition. Because anion exchange resins are quite selective for sulfate ion, the presence of sulfate in raw water decreases the efficiency of the resin to absorb nitrate. It was found in this study, however, sulfate was easily removed from the spent resin by the sodium chloride regenerant in nearly stoicheometric proportions whereas excess regenerant is required for nitrate removal. Sulfate, by preventing a large build up of nitrate on the resin, promotes low nitrate leakage from a partially regenerated column. The overall effect of sulfate, however, is to increase the salt required to remove a unit quantity of nitrate per unit quantity of water treated. This study also confirmed that large quantities of regenerant (20 pounds per cubic foot of resin) are required to remove most of the nitrate from the spent resin. Not all nitrate need be removed, however, to reduce nitrate levels in treated water to below 45 ppm.

For McFarland wells, the salt requirements for lowering nitrate levels to between 30 and 45 ppm ranges between an estimated 2.48 pounds to 4.48 pounds per cubic foot of resin. The costs range between 2.31 cents for 1,000 gallons of blended (50/50) water (or $7.56 per A-F) for Well 2 to 12.28 cents per 1,000 gallons of treated water (or $40.02 per A-F) for Well 3 water. Well 3 represents a particularly difficult water to treat as nitrate levels are near 100 ppm and sulfate levels are above 300 ppm. Nitrate levels in Well 2 are near 60 ppm and sulfate levels are near 200 ppm. Salt requirements for waters of other compositions are given. (Table A-13 Appendix.)

7. To achieve efficient nitrate removal, good brine and influent flow distribution are essential and may require modification of commercially available softening equipment. A method of declassification (thorough mixing) of the resin after downflow regeneration should also be incorporated in the regeneration cycle.

8. Wastewater is produced during the regeneration cycle having an enriched composition of sodium sulfate, chloride, and nitrate. Continuous operation of Well 2 would produce over

12,000 gallons of wastewater per day (see Figure 1). Continuous operation of Well 3 would produce an average of 38,686 gallons of wastewater per day.

9. An R.O. system was operated on Well 3 for over 1,000 hours. The system contained spiral wound cellulose acetate membranes and produced 15 gpm of treated water with 75 percent water recovery.

Of the major groundwater anions, nitrate is the most difficult to remove by R.O. During the operation of the system, nitrate passage rose from 33 to 65 percent.

10. Operation of the R.O. system was plagued with several annoying electrical and mechanical failures which required considerable amount of downtime, maintenance, and servicing. This experience makes the use of R.O. questionable for well site removal of nitrate in small communities with little or no maintenance personnel.

11. The most serious trouble experienced with the R.O. system was failure of O-ring seals between the high pressure brine and low pressure product channels. This was presumably due to lateral movement of membrane elements during system start and stop required to follow start and stop of the well pump. This difficulty can be avoided by providing sufficient well site storage to allow continuous system operation.

12. Capital equipment costs for treating water by R.O. for nitrate reduction from a 1-mgd production well are over $800,000. Estimates of water costs including amortized equipment and operating and maintenance costs are 99.2 cents per 1,000 gallons of water produced (26.2 cents per cubic meter or $323.29 per A-F).

13. Twenty-five percent of the well capacity becomes waste brine from the R.O. system. For a 1-mgd well, 250,000 gallons of wastewater are produced per day. This quantity would use one-half of the municipal waste treatment capacity of McFarland's wastewater treatment plant and would add approximately 2 tons of dissolved solids per day to the local disposal area if operated at McFarland's Well 2. (Compare to 1 ton for ion exchange--same basis.) However, no sodium chloride is brought into the community to operate the system.

14. The advantages of R.O. over ion exchange are that fewer processing chemicals need be brought into the locale and considerable demineralization of product water is achieved.

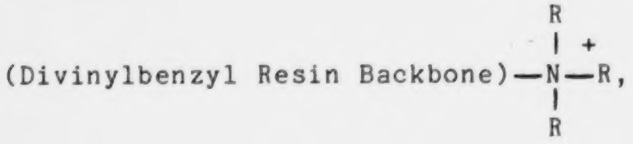
15. For small communities, there appears to be few advantages to using R.O. followed by ion exchange polishing to produce water of low nitrate content (less than 5-ppm nitrate).

Use of R.O. brine generated on Well 3 water was found to be ineffective for regenerating the nitrate-loaded resin; consequently, some salt is still required. The added complexity and cost of operating an R.O. system in conjunction with ion exchange at the well site appears to outweigh any cost advantages which could be gained. Water costs by operation of such a system are estimated to be at least $1.11 per 1,000 gallons of low nitrate content water which could be blended with other well water. If blended (one volume raw water to two of treated water), cost per 1,000 gallons would be 74 cents per 1,000 gallons plus brine disposal costs. Resin regeneration requirements would be substantially reduced to below 10 percent of their value if ion exchange alone would be used. Volume of wastewater would be about 115,000 gallons of mainly R.O. brine per mgd of blended product.

16. R.O. followed by ion exchange may be cost effective for large scale systems which were not a subject of this investigation. Economies of scale could lower R.O. costs and advantages of demineralization may be highly desirable. Large communities with high nitrate, high TDS groundwater can treat with R.O. and polish by ion exchange and could blend the product with high nitrate - high TDS water and may find the process cost effective.

THEORETICAL ASPECTS

1. A special series of strong-base anion exchange resins, synthesized especially for this program, shows a striking correlation between nitrate-to-sulfate selectivity and the molecular structure of the alkyl substituents on the quaternary amine ion exchange sites. Some of the resins are nitrate-to-sulfate selective. The normal increasing order of ion selectivity for anion exchange resins at normal groundwater concentrations is bicarbonate, chloride, nitrate, sulfate. As the number of carbon atoms in the R groups around the nitrogen increases in the resin structure,



$$\text{(Divinylbenzyl Resin Backbone)}-\begin{array}{c} R \\ |\;^{+} \\ N \\ | \\ R \end{array}-R,$$

the increasing order of ion selectivity is changed to bicarbonate, chloride, sulfate, nitrate. Where R is methyl K_S^N (a measure of nitrate-to-sulfate selectivity) is approximately 100; whereas if R is ethyl, K_S^N is approximately 1,000. Thus, in column tests with the triethyl resin on water having a nitrate plus sulfate concentration of about 10 meq per liter, nitrate is the last ion to break through. Other resins with a total of four and five carbon atoms show intermediate

K_S^N values. The effect of introducing OH groups into the alkyl substituents is to decrease the K_S^N value. For example, if the R groups are ethoxy, the K_S^N value is approximately 10.

These structural effects on K_S^N value are ascribed to steric strains set up in the resin by the spacial (or steric) requirements of the alkyl R groups with nitrate having capability of decreasing the steric strain while sulfate can increase strain. Little effect on the K_C^N values are noted. All resins are easily regenerated with chloride brines. This observed effect of molecular structure gives rise to a concept of structurally induced electroselectivity reversal.

2. The net effect of using the triethyl amine resin when compared to the commercially available trimethyl resin is to increase the bed life BV(N) from of 170 to 275, an increase of 62 percent, treating a water containing 1.5 meq nitrate and 6.5 meq sulfate per liter. The immediate effect is to reduce wastewater for processing by 38 percent. A second desirable effect of using the triethyl resin is to reduce the amount of regenerant required to remove an equivalent amount of nitrate by 25 to 50 percent depending on the mode of operation and level of regeneration selected. This represents a projected cost savings of $84,000 to $168,000 in salt over the 20-year plant life plus at least equivalent amounts for brine disposal costs. Special column operation must be used since the nitrate breakthrough can be compound and a choice is available to operate to the first or second nitrate breakthrough. A third advantage in using NSS resins is to preserve more of the raw water quality by allowing sulfate to pass through the column.

3. The structural effects noted above were found characteristic of a series of eight special resins which show a trend toward increased K_S^N (and greater process efficiency) without any observable limit. Consequently, it is believed a continuing study of structural changes can produce an optimum resin which will give an even greater cost saving than noted above.

4. The NSS resins have characteristics which require special consideration in process design.

a. Anion exchange capacity is approximately 15 percent lower than the Type 1 counterpart.

b. Two nitrate breakthrough points are obtained with partially regenerated resin. Nitrate leakage prior to the first is determined by chloride ion-nitrate ion competition for resin sites. The first breakthrough point occurs simultaneously with sulfate breakthrough. Nitrate leakage after sulfate breakthrough is determined by nitrate ion-sulfate ion competition. The first break is usually sharp; the second is not.

c. To use the triethyl NSS resin effectively, two columns can be run out of phase to average the two levels of nitrate leakage. The use of a polishing bed may also be required.

5. The method used to discover the nitrate-to-sulfate selective resins was through observation and analysis of (a) column breakthrough profiles and relation to chemical structure; (b) departure of column behavior from a mathematical model; (c) the shape of binary isotherms; (d) effect of structural changes on primary, secondary, and tertiary ammonium weak-base resins; (e) swelling effects of ions on resins; (f) experiments on nitrate-selective sulfate-loaded resins; and (g) inferences from physical organic chemical studies of effects of structure on chemical equilibrium. This method may be applied to studies on selective removal of other inorganic contaminants.

6. Nitrate-to-sulfate selectivity among strong-base resins was found to also increase with the degree of resin cross linking. The list of resins studied in increasing order of nitrate-to-sulfate selectivity are

Duolite A-101D
Duolite A-104
Amberlite IRA-910
Dowex SAR
Amberlite IRA-900

The literature shows IRA-410 and Ionac A-550 as well as some tertiary amine weak-base resins to have nitrate-selective tendencies. However, commercially available resins do not show enough nitrate selectivity to be of significant value. In terms of this study they are not NSS resins. Lower anion exchange capacity is a disadvantage of the higher cross linked resins and also makes the ion exchanger appear to be nitrate-to-sulfate selective through the electroselectivity effect. (Activated carbon is a noteable case.) Also, where nitrate and sulfate are equal in selectivity, the spent column will have nitrate evenly distributed in the column. This is a disadvantage in regeneration since nitrate must be moved through the entire column. Consequently, A-101D resin was chosen for pilot studies because nitrate concentrates near the exit end of the column from which it is more easily removed during regeneration. It is also pointed out in the study that threshold K_S^N values must be reached before a resin can be a nitrate-to-sulfate selective resin and before process efficiency can be improved.

7. Use of chemical regenerants other than sodium chloride was briefly explored. It was demonstrated that nitrate can be selectively removed using sulfate-loaded resins. It is suggested that dilute calcium sulfate be tested as a regenerant. Larger volumes of regenerant using a low TDS water are required.

Such a supply is available in McFarland as irrigation water. Waste brine would contain calcium nitrate and sulfate both of which are disposable to agricultural lands. Ammonium chloride is also suggested as regenerant which would give ammonium nitrate and sulfate as a disposable brine.

8. From these studies and a review of previous studies on synthesis of resins with higher nitrate-to-chloride selectivity, it does not appear regenerant requirements can be reduced if nitrate-to-chloride selectivities are increased. Available anion exchange resins are already nitrate-to-chloride selective and difficult enough to regenerate to the chloride form. Making them more selective for nitrate will only add to further regeneration inefficiencies. This, however, does not appear to be the case with the NSS resins since the nitrate-to-chloride selectivities did not change substantially whereas nitrate-to-sulfate selectivity did change.

RECOMMENDATIONS

1. A demonstration plant of 1/2-mgd to 1-mgd capacity should be installed and operated to obtain actual operational experience regarding reliability, health, safety, and costs.

Although the ion exchange process has been used many years in industrial applications and hardness removal from domestic supplies, no significant operating experience has been obtained on a full-scale domestic system for nitrate removal. Use of the process for this purpose cannot be considered as a standard engineering application until the process has been successfully demonstrated on a full scale.

A single-bed plant with downflow partial regeneration should be used. Commercially available resins should be employed as further testing of the NSS resins is required before application.

2. As pointed out above, the cost of regenerant and brine disposal over the plant lifetime can be several times the cost of the plant. Efforts should be made to reduce regenerant requirements to the lowest level practicable. This can be done by recycling portions of brine and brine rinse as well as backwash waters in demonstration plant operation and continuing studies on NSS resins.

3. Studies should be conducted on use of regenerants for the single-bed process other than sodium chloride to produce waste brines more amenable to disposal on agricultural land.

4. Studies on NSS resins should continue since further increases in nitrate-to-sulfate selectivity can be expected. These resins must also be characterized as to fouling tendency, chemical degradation, and acceptance in water treatment.

5. Brine disposal is the single most important factor which deters widespread use of the ion exchange process. All future efforts to improve the process should focus on this impediment to its application.

6. R.O. is not recommended for nitrate removal at remote well sites in small communities because of cost and operational problems.

SECTION 3

REVIEW OF PREVIOUS WORK

EARLY RESEARCH WORK - GAUNTLET

A review of work on nitrate removal by strong-base ion exchangers is given by Gauntlet (Reference 2). Earliest work reported included work by Delius (Reference 3) and Rummel (Reference 4), Korngold (Reference 5), Midkiff and Weber (Reference 6), Fresenius (Reference 7), and Vlasak (Reference 8). These cited works showed that irrespective of resin used sulfate ions were adsorbed more strongly by the resins. Using various resins and waters of varying nitrate and sulfate composition in column tests, it was demonstrated that resin capacity for nitrate decreased with increasing feedwater sulfate content. Gauntlet compared the chemical efficiency of complete column regeneration with partial regeneration and found much better efficiency for partial regeneration for high sulfate waters and moderate improvement for low sulfate waters. He reported cost estimates ranging from 0.55 to 0.8 pence per cubic meter (approximately 6 cents per 1,000 gallons) depending on sulfate content. The details of this cost estimate were not given. Gauntlet compaired single bed to a continuous loop system and pointed out the comparatively lower resin requirements and constant quality product of the latter. He believes complete regeneration of a single bed to have the disadvantage of producing a corrosive high chloride to alkalinity ratioed product.

GARDEN CITY PARK, NEW YORK PLANT

An ion exchange plant for nitrate removal was put into operation in 1969 in Garden City Park, New York (Reference 9). The plant uses a strong-base anion exchange resin in a continuous flow loop system (Reference 10). The plant capacity is 1,200 gpm and had a total cost of $700,000. Unfortunately, there are no operating costs or experience reported on this plant. It is understood the plant has only been operated for a short time since its installation. The influent water has a composition in mg/l of nitrate nitrogen = 14.9, chloride = 25.5, alkalinity = 18, TDS = 197, and specific conductance = 330 mmhos. No sulfates are reported but are believed to be quite low.

The design of the plant is based on studies performed with a continuous loop ion exchange pilot plant (Reference 11). Pilot studies were also made on Long Island well water from Bethpage Water District, New York (Reference 12). Basic design criteria developed were:

1. Flow rate = 50 gpm/square foot of bed cross-section.
2. Nitrate utilization of resin = 0.4 equivalents per liter of resin.
3. Salt consumption of 1.0 to 2.5 pounds per 1,000 gallons of water for reduction of nitrate (nitrogen) by 10 to 20 ppm.

MIDKIFF AND WEBER

Midkiff and Weber (Reference 6) performed significant work on nitrate removal with Dowex 21K strong-base anion resin. Column operation was examined for hydraulic loadings ranging from 6.5 gpm per square foot to 59 gpm per square foot for a water containing both nitrate and sulfate. No significant difference in breakthrough profiles could be attributed to changing flow rate within this range. They caution, however, not to generalize these results. They also investigated effect of bed depth and found anions were exchanged at extremely rapid rates giving a reaction zone for nitrate ion of about 14 cm and a theoretical contact time of 7.4 seconds. They suggest that with the resin used a bed depth of 30 inches is sufficient to establish and stabilize a reaction profile for all ions studied.

KORNGOLD

Korngold (Reference 5) reports experiments with Amberlite-400 and high chloride, low sulfate nitrate laden waters. His results show typical breakthrough curves for the four major anions. Of major interest is his brief study on use of seawater as a regenerant.

EPA RESEARCH

Buelow et al. (Reference 13) investigated a reported nitrate selective resin and how specific anions interfere with anion resins in nitrate removal service. The Dowex 21K which was reported as "nitrate selective" by Chemical Separations Corporation did not show nitrate selectivity in waters of TDS concentrations of about 500 ppm. At high TDS levels, the resin did show nitrate selectivity. This was pointed out to be expected because of the monovalent ion preference in feedwaters of high ionic concentrations. A discussion of the "electroselectivity" effect was given in Reference 1. Sulfate, iron, and silica were pointed out to be the most problematical for nitrate removal by the Dowex resins. Sulfate ion was the major interfering substance since it replaced the nitrate ion on the resin. Cost estimates were also given. Operating cost estimates ranged from 16 cents to 17 cents per 1,000 gallons. Salt and brine disposal costs were 51 and 64 percent of total costs. Operating and capital amortization were estimated from 12.5 to 21.5 cents per 1,000 gallons.

CLIFFORD

Clifford (Reference 14) has closely examined a two-bed process using a strong acid cation exchanger followed by a weak-base anion exchanger. Regeneration avoids the use of sodium chloride with use of nitric acid and ammonium hydroxide; ammonium nitrate in the waste product is disposable as a fertilizer.

This process has advantages of also softening the water and effecting some demineralization. Clifford's study was mainly concerned with the second part of the process using the weak-base anion resin, because resins with high nitrate to sulfate selectivity were most desirable. For that reason, an exhaustive study was made comparing the ionic selectivities of 19 strong-base and 13 weak-base resins. He found that for groundwaters having TDS concentrations up to at least 3,000 ppm all resins preferred sulfate to nitrate. Of major interest in this work is a statistical analysis of the data to pinpoint resin properties which determine nitrate selectivity.

Also of importance is a review of previous attempts to make nitrate-selective resins. These include attempts by Grinstead et al. (Reference 15) who proposed the use of a resin without functional groups into which was adsorbed a nitrate selective analytical reagent (amidine). Disadvantages were low capacity and loss of amidine to process streams. Other attempts reviewed are by Meloan (Reference 16) (and more recently Meloan and Danen) (Reference 17) and Wallit and Jones (Reference 18). The former prepared polymers incorporating nitrate-selective organic reagents and the latter prepared a polymer with salinogen functional groups; neither approach was satisfactory.

Clifford's work was most useful in stimulating the study reported in Section 8 of this report. Further discussion of this work is given there.

TEST PLANTS

Green et al. (Reference 19) report on a proposed two-year program to operate ion exchange plants by the Anglian Water Authority. One plant design incorporates two single-bed ion exchange shells which run out of phase to offset treated water quality variations. Treated water is further blended with untreated water prior to chlorination and distribution. Counter current total or partial regeneration is proposed. The plant will treat 39 m^3/hour (172 gpm) with an estimated waste of 15 to 45 m^3/day (3,960 to 11,880 gpd).

The capital cost is estimated as 90,000 pounds (approximately $180,000) with treatment costs estimated at 0.8 p/m^3 (approximately 6 cents per 1,000 gallons).

Effluent disposal and transportation costs are estimated at a maximum of 21,900 pounds (approximately $43,800) per annum.

A second test plant is based on a continuously operating closed-loop design having a capacity of 0.9 mgd. A brine waste of 1,122 gpd is produced and will be disposed at a nearby estuary. The capital cost is 120,000 pounds (approximately $240,000) and an estimated operating cost is 1.3 p/m^3 (approximately 9.8 cents per 1,000 gallons). Effluent disposal costs are estimated at 10,000 pounds per year (approximately $20,000 per year). Effluent disposal is viewed as the major problem and the subject of future research programs.

DALTON

Dalton (Reference 20) studied the application of nitrate removal by ion exchange to waters in the Republic of South Africa and southwest Africa.

Amberlite IRA 904 resin was selected from 32 resins as having highest nitrate-to-sulfate selectivity and was used in pilot plant tests. The waters tested were of high TDS allowing electroselectivity effects to give high nitrate-to-sulfate selectivity. Treatment costs given are for small systems to meet a nitrate standard of 90 ppm.

SECTION 4

TEST AREA EQUIPMENT AND PROCEDURES

WELL 3, McFARLAND, CALIFORNIA

All tests were conducted at Well 3 owned and operated by the McMWCo. Water quality at this and other wells in McFarland is discussed in the last part of this section. Because of the high nitrate level of this well, it was not connected to the municipal supply and was only available for this research work. The well site is shown in Figure 2.

The pump capacity is approximately 1 mgd. A hydropneumatic tank of approximately 10,000 gallons, piping, and pump are shown in Figure 2. These facilities were located on a lot approximately 80 by 65 feet with adequate space for the site improvements constructed for this study (Figure 3). These improvements were designed to accommodate equipment for conducting both the field tests and laboratory scale experiments. Water was supplied directly to a concrete pad and trailer from the hydropneumatic tank. All product and wastewaters were discharged from the pad directly into the city sewer system. The 30-foot by 32-foot pad was large enough to accommodate a field-test ion exchange system, a field-test R.O. system, and a single-module R.O. system with the necessary tanks for temporary water storage. A trailer adjacent to the pad housed a field office and limited laboratory facilities. An industrial steel roof was installed over the entire concrete pad.

LABORATORY ION EXCHANGE COLUMNS

Laboratory ion exchange columns were fabricated from 4-foot lengths of 2-inch-ID acrylic resin pipes and PVC FLO-CONTROL adapters used as end fittings (Figure 4). A Masterflex Model 7017 was capable of delivering up to 1,350 ml per minute through a 24-inch bed of resin in the 2-inch-ID columns (1 bed volume = 1,245 ml). A source of Well 3 water was available in the trailer. Synthetic mixtures were prepared and pumped directly at measured flow rates with the Masterflex pump through the ion exchange columns.

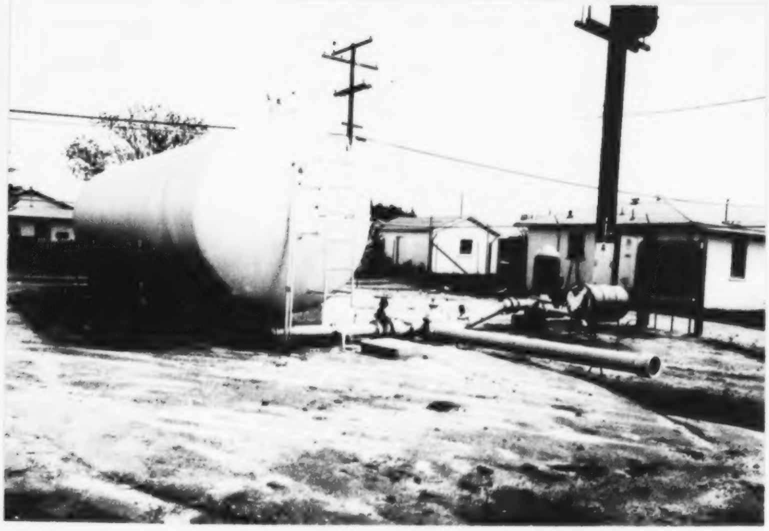


FIGURE 2 WELL SITE NO. 3 McFARLAND CALIFORNIA

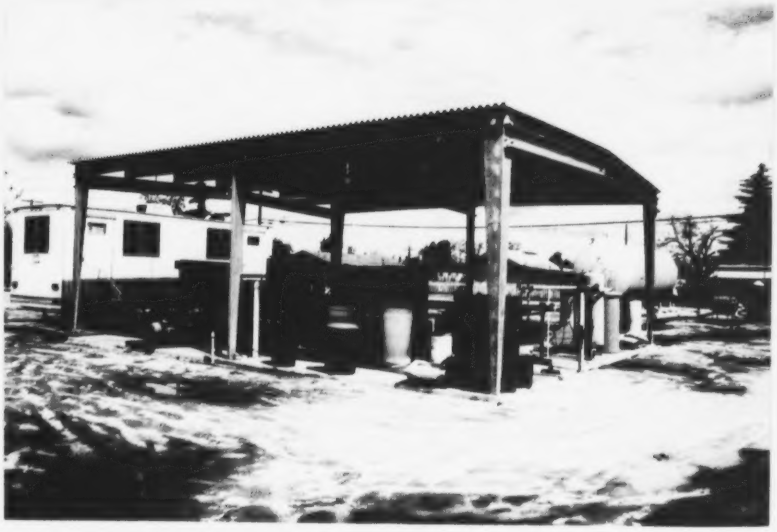


FIGURE 3 : SITE IMPROVEMENTS AT WELL SITE NO. 3

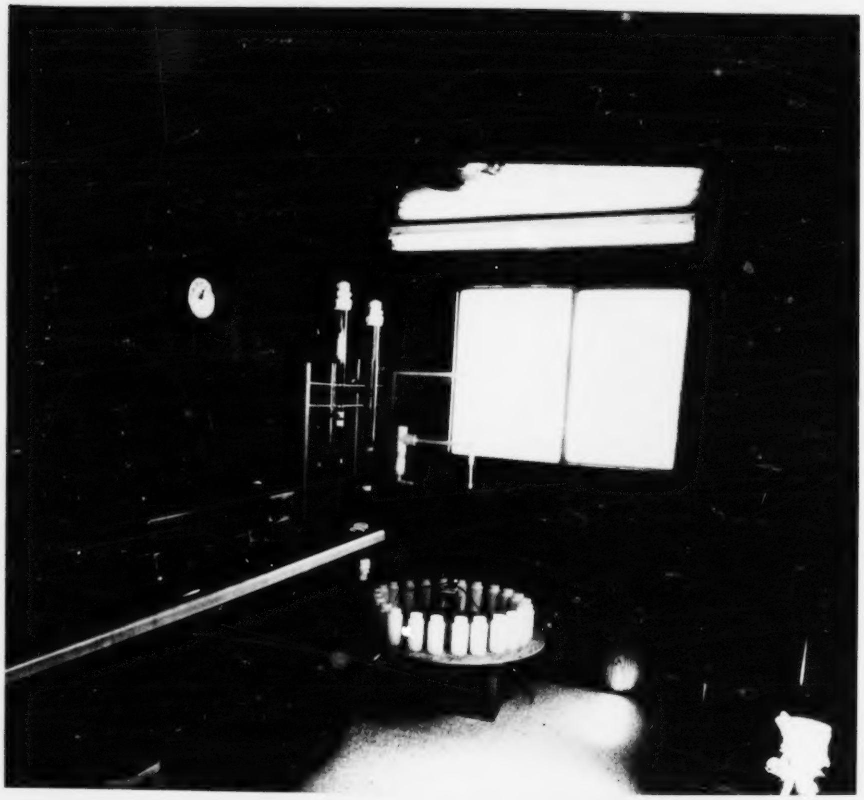


FIGURE 4 : LABORATORY ION EXCHANGE COLUMNS

PILOT ION EXCHANGE COLUMN - DESCRIPTION

A Culligan HI-FLO 5 Water Softener Model 150 was installed on the pad at Well 3 (Figure 5). A sketch of the system is shown in Figure 6. The completely automatic water softener was converted to a semiautomatic anion exchanger by installing an industrial timer and anion exchange resin (Duolite A-101D). Six hydraulic valves controlled by a motor-driven pilot valve determine various cycles of operation including service, backwash, brine rinse, and fast rinse. An industrial timer was installed for selection of duration for the latter three cycles. The service cycle duration can be controlled by a clock mechanism allowing regeneration as frequently as 12 hours or can be manually set to allow shorter service cycles (see Figure 7).

The system was connected directly to the Well 3 water supply by 1-inch PVC pipe. Replumbing to 2-inch pipe was later found necessary to gain maximum flow rates of 6 cfm during the service period.

A flowmeter was connected to the outlet pipes which discharged directly to a drain. Inlet and outlet pressure gages and control valves were also installed. Plumbing provisions were also made to allow the ion exchanger to treat the product from the pilot scale R.O. system.

Duolite A-101D (4.36 cubic feet), a Type I resin, was placed in the 20-inch-diameter resin tank. This was sufficient resin to provide 24 inches of bed depth. It was found that during the 10-gpm backwash, some resin was thrown into the drain line. Backwash rate could be decreased but not without affecting the brine draw mechanism. A 50-mesh stainless-steel screen was installed in the feed inlet at the top of the tank (through which the backwash water exits) to prevent resin loss and backwash rate was left at 10 gpm. Salt was charged to the brine tank manually, and water was automatically fed to the tank at a predetermined flow rate during the service cycle. An adjustable timer controlled the time of charging water to the tank (up to 60 minutes). During regeneration, most of the saturated brine was drawn from the brine tank by an eductor. The brine mixed with water in an approximate ratio of one part brine to two parts water and downflowed over the resin. Thus the amount of salt used for regeneration was indirectly determined by the amount of water flowing into the brine tank during the service cycle. The manufacturer provides a table relating time of filling the brine tank to amount of salt used in regeneration. This was not the most efficient system for research purposes where it is desirable to know more exact amounts of salt used. Consequently, the brine draw system was later altered as described in Reference 1. Section 6 of this report reviews modifications made to the flow distribution system.

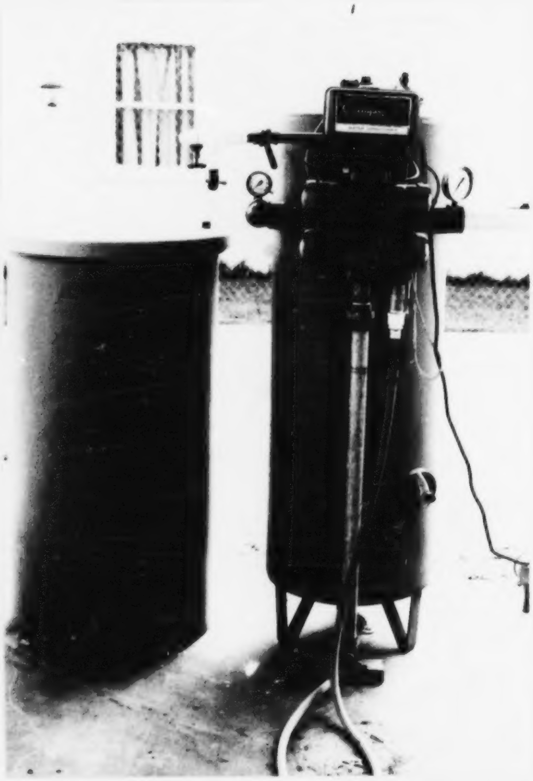


FIGURE 5: PILOT ION EXCHANGE COLUMN

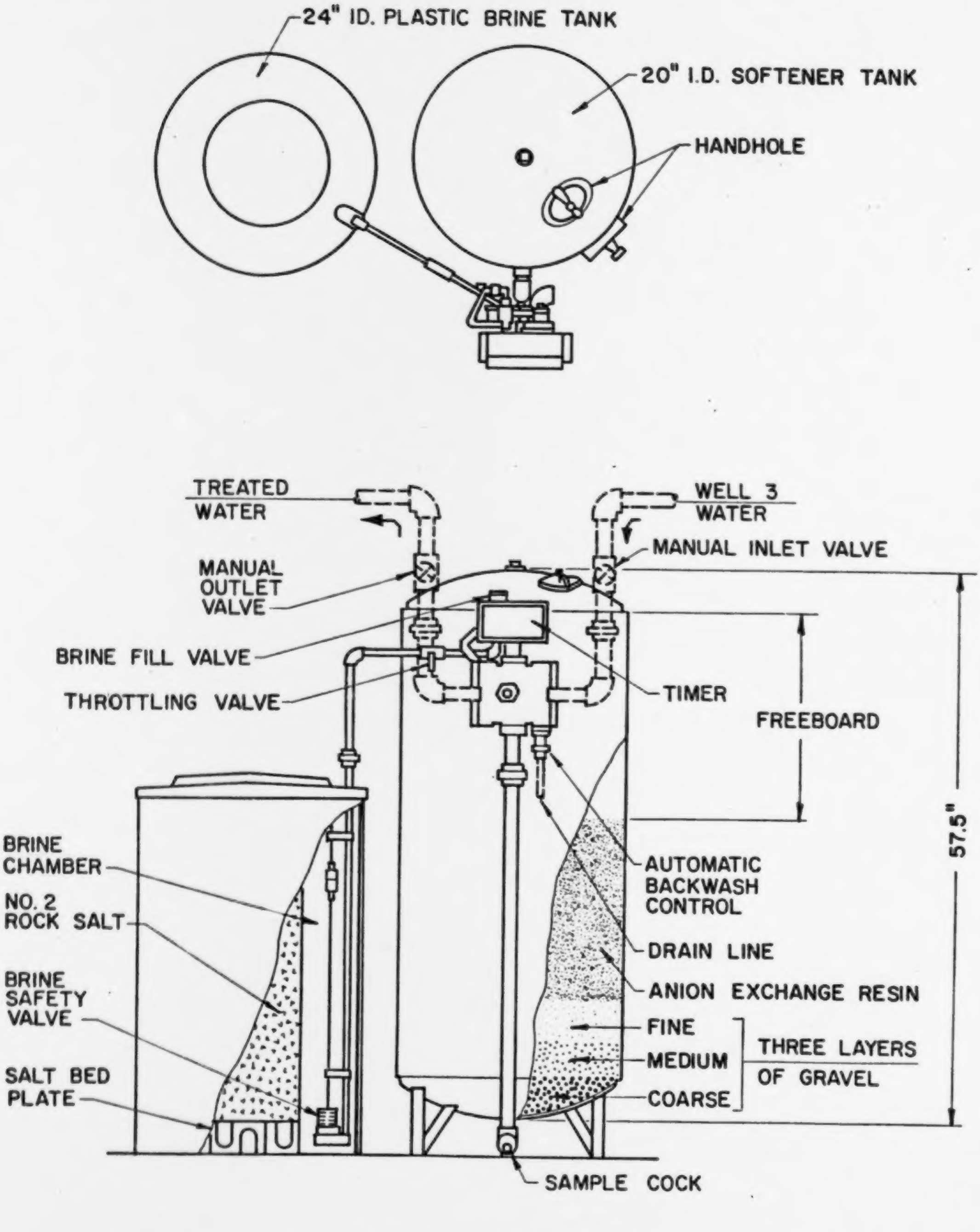

24" ID. PLASTIC BRINE TANK
20" I.D. SOFTENER TANK
HANDHOLE
TREATED WATER
WELL 3 WATER
MANUAL INLET VALVE
MANUAL OUTLET VALVE
BRINE FILL VALVE
THROTTLING VALVE
TIMER
FREEBOARD
57.5"
BRINE CHAMBER
NO. 2 ROCK SALT
AUTOMATIC BACKWASH CONTROL
DRAIN LINE
ANION EXCHANGE RESIN
BRINE SAFETY VALVE
FINE
MEDIUM
COARSE
THREE LAYERS OF GRAVEL
SALT BED PLATE
SAMPLE COCK

FIGURE 6 HI-FLO 5 WATER SOFTENER SYSTEM

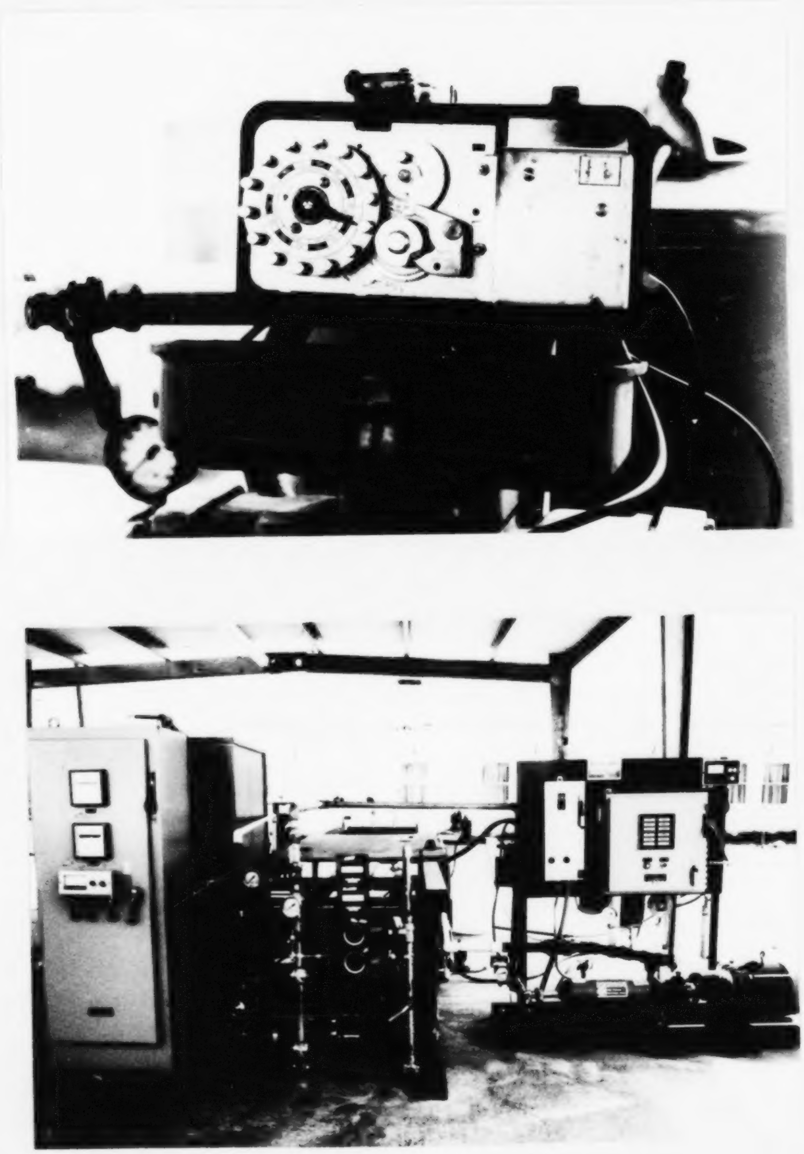


FIGURE 7 : VISUAL COMPARISON OF CONTROLS FOR TWO SYSTEMS - ION EXCHANGE (UPPER) - R.O. (LOWER)

SINGLE-MODULE R.O. SYSTEM - DESCRIPTION

A small R.O. system was purchased for use on this program to test nitrate removal characteristics of five different membrane types. The system is shown in Figure 8. A flow diagram is given in Figure 9. In Figures 9 through 13, the following schematic symbols are used:

P, PI, P1, P2, etc. = pressure gage.
PS, PR = pressure-activated switch or regulator.
F1 = flow rate indicator.
SDI = silt density index apparatus.
H^+ = acid feed tank.
Cl_2 = chlorine feed tank.
S = Sample port.

Only one element could be run at a time. Since the five elements were all different, conditions for their operation differed. The Dow and the DuPont units are hollow fiber elements and housed in their respective pressure vessels. The three spiral wound elements were interchangeable in one pressure vessel. The Goulds pump mounted on the skid handled the different flows required. Two flowmeters were installed to cover the different flows. A recirculation/feed tank was provided to allow more than a once through operation and provide for pretreatment.

The membrane elements tested included those listed in Table 1.

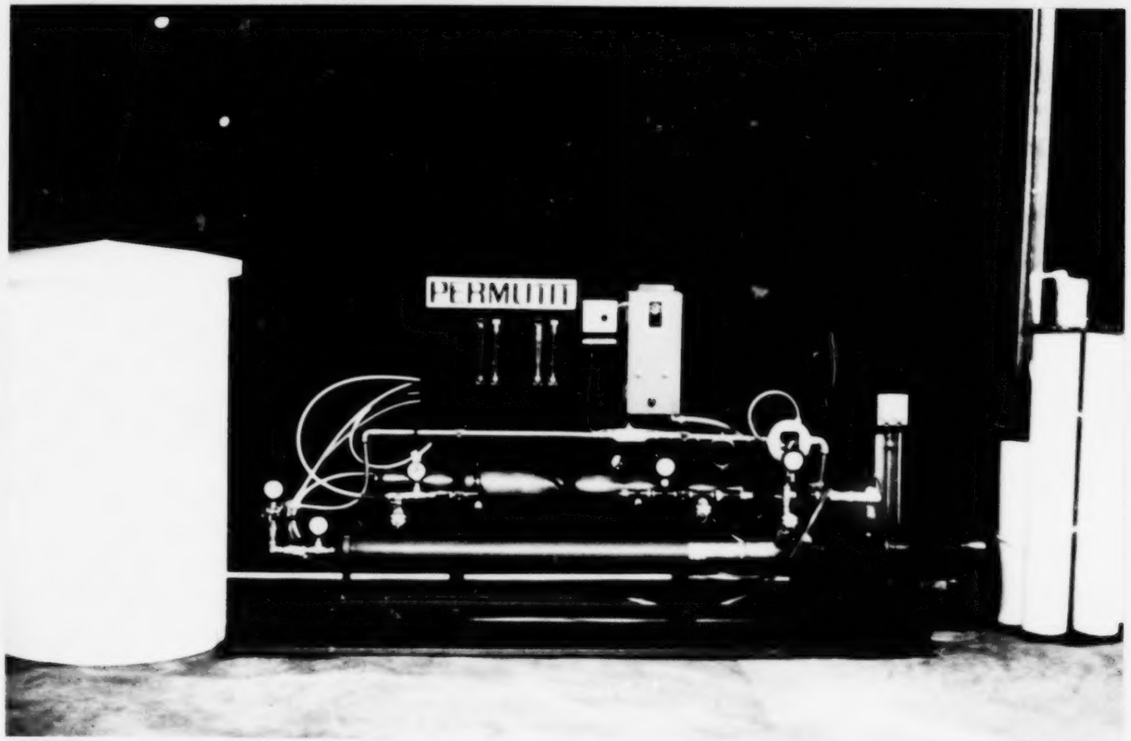


FIGURE 8 : SINGLE MODULE REVERSE OSMOSIS SYSTEM

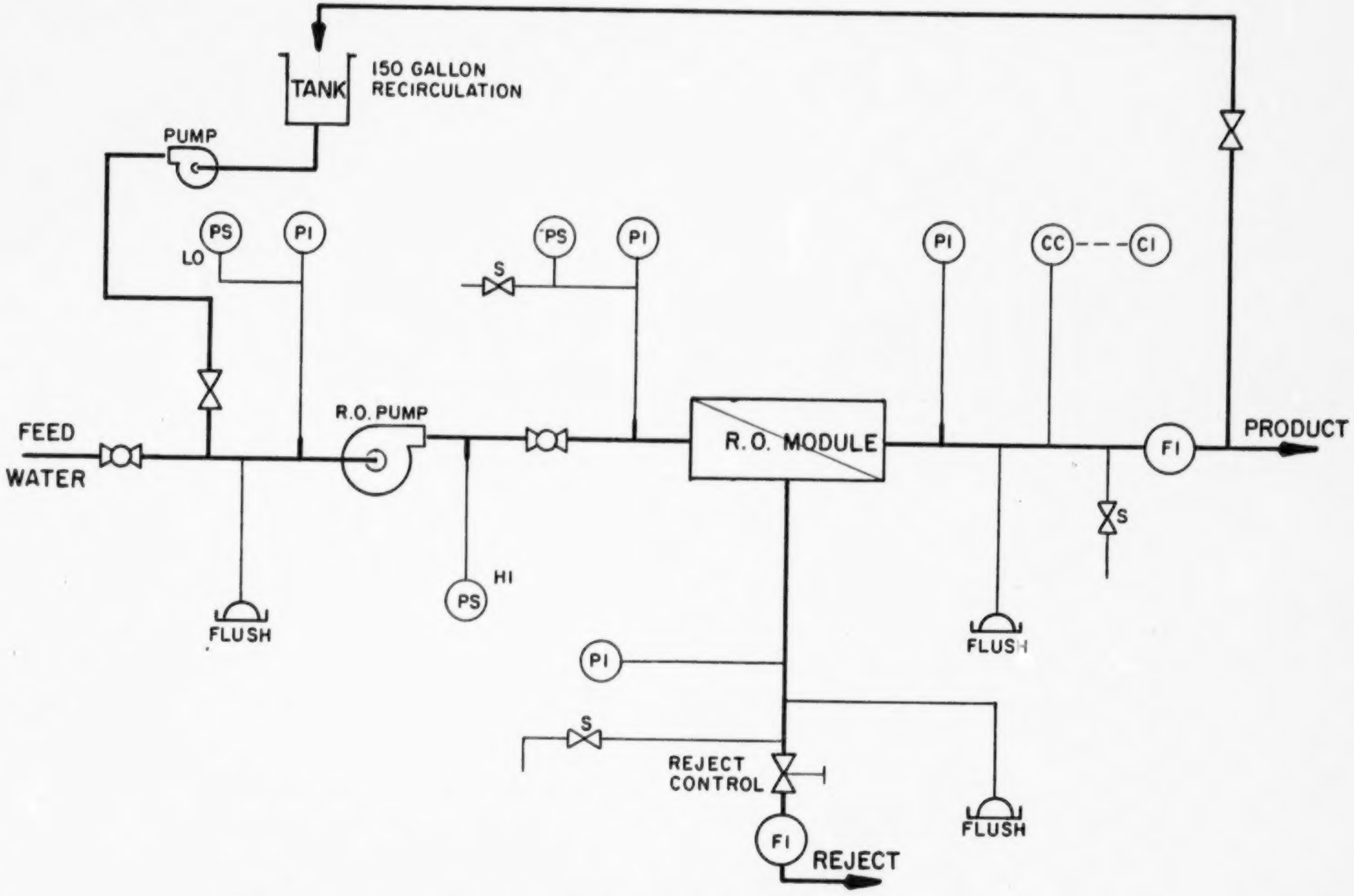

150 GALLON
RECIRCULATION
TANK
PUMP
PS
LO
PI
PS
S
PI
PI
CC
CI
FEED
WATER
R.O. PUMP
R.O. MODULE
FI
PRODUCT
S
FLUSH
PS
HI
FLUSH
PI
S
REJECT
CONTROL
FI
REJECT
FLUSH

FIGURE 9 SINGLE MODULE R.O. SYSTEM

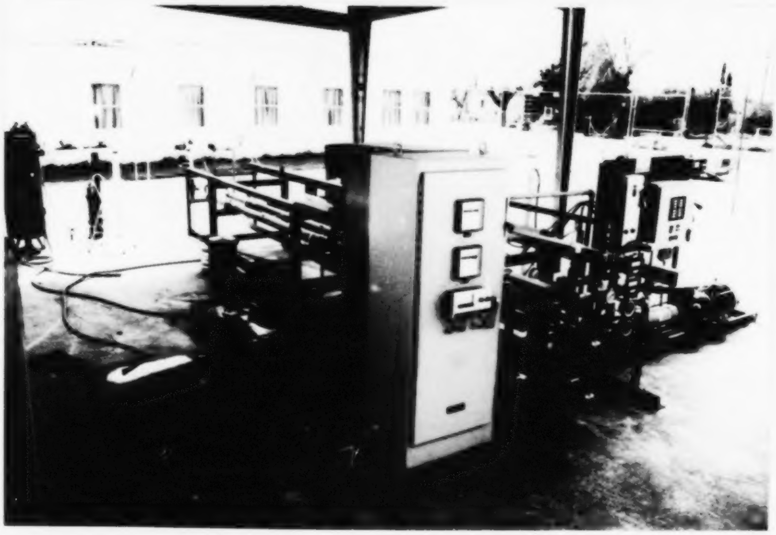


FIGURE 10 : PILOT REVERSE OSMOSIS SYSTEM

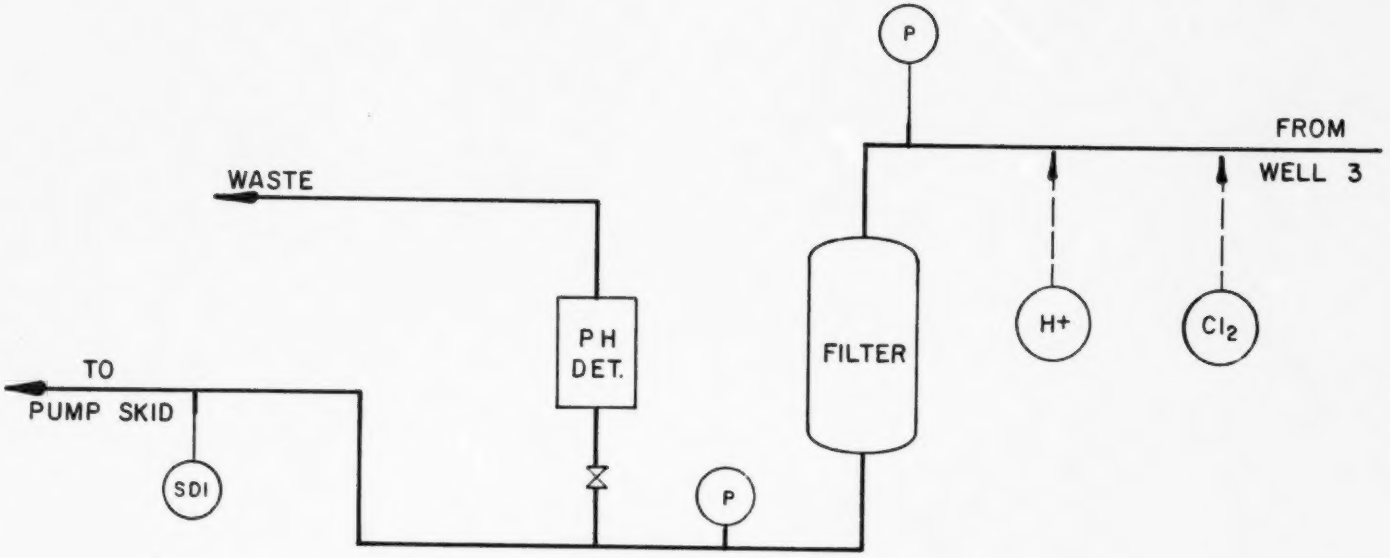

FROM
WELL 3
P
Cl_2
H+
FILTER
P
PH
DET.
WASTE
TO
PUMP SKID
SDI

FIGURE II : REVERSE OSMOSIS PRETREATMENT SYSTEM

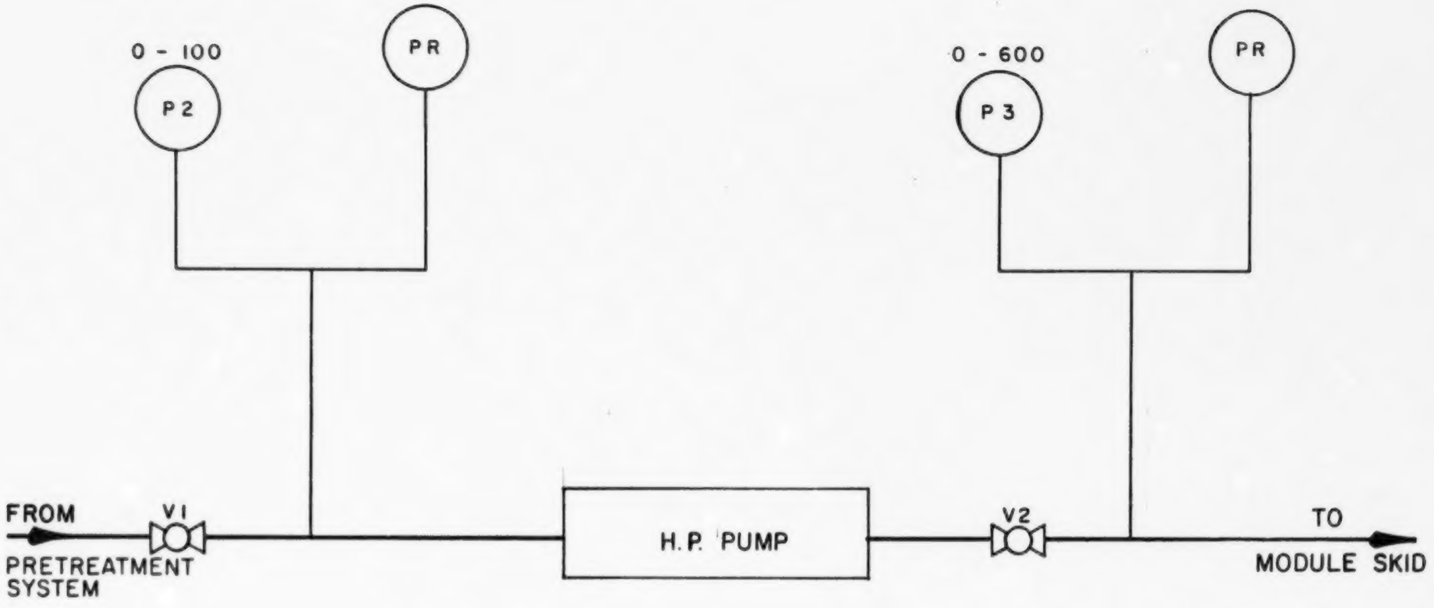

0 - 100
P2
PR
0 - 600
P3
PR
FROM
PRETREATMENT SYSTEM
V1
H.P. PUMP
V2
TO
MODULE SKID

FIGURE 12 : REVERSE OSMOSIS PUMP SKID

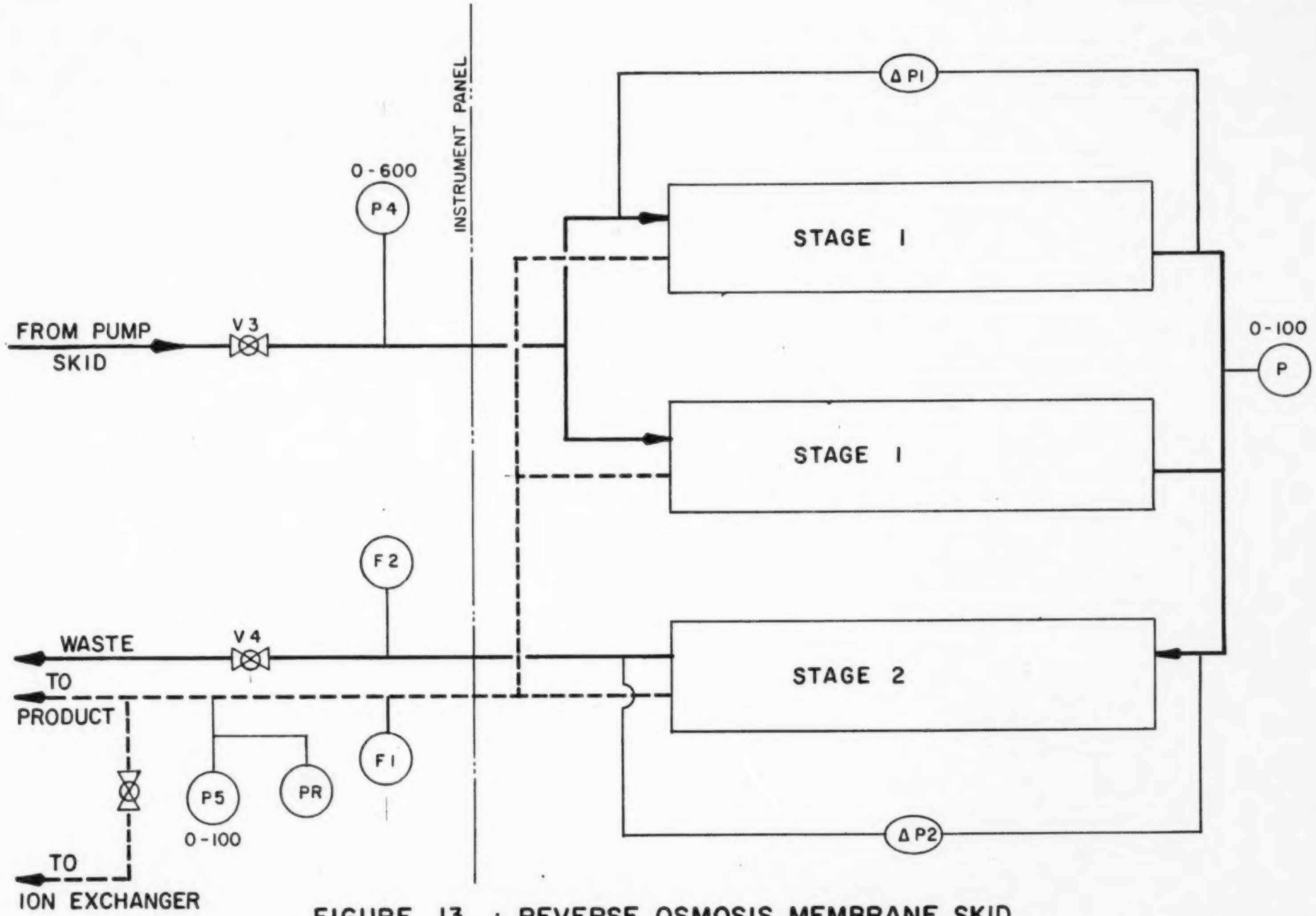

INSTRUMENT PANEL
0-600
P4
FROM PUMP
SKID
V3
ΔP1
STAGE 1
STAGE 1
STAGE 2
0-100
P
F2
WASTE
V4
TO
PRODUCT
F1
P5
0-100
PR
TO
ION EXCHANGER
ΔP2

FIGURE 13 : REVERSE OSMOSIS MEMBRANE SKID

TABLE 1. MANUFACTURER'S DATA FOR R.O. MEMBRANES

Element	Membrane Type	Operating Pressure	Feed Flow Rate (gpm)	Product Flow Rate (gpd)	Percent NaCl Rejection
ROGA 41606	CA-SW	400	12	12,000	95
ROGA	CA-SW	200	NS	NS	NS
ROGA 4600 PA	PA-SW	400	NS	1,250	98
Permasep 0420-021	PA-H.F.	400	3.3	2,100	90
Dowex RO.25K	CA-H.F.	200	1.7	250	90

CA = cellulose acetate
SW = spiral wound
PA = polyamide

NS = not specified
H.F. = hollow fiber

PILOT R.O. SYSTEM - DESCRIPTION

The pilot R.O. system used for tests on nitrate removal is shown installed on the pad at Well 3 in Figures 7 and 10. Flow diagrams are given in Figures 11, 12, and 13. Physically the complete system was comprised of a pretreatment system, a pump skid with control panel, a membrane skid, and instrumentation panel.

Pretreatment System

The pretreatment system consisted of a chlorine feed system, an acid feed system, and a micron filter. The chlorine feed system consisted of a 40-gallon supply tank and chemical feed pump (Precision Control Products Series 10,000). The chlorine supply was prepared from well water and granular sodium hypochlorite. The rate of injection of the chlorine solution was adjusted on the feed pump to give 1/2- to 1-ppm Cl_2 in the feed stream. The acid feed system consisted of a 40-gallon tank and a similar chemical feed pump.

An approximate 10 percent (by volume) solution of sulfuric acid was prepared in the tank and rate of feed adjusted to give a pH varying between 4.0 and 5.8. Although level sensors were supplied with the feed tanks, they were not used because of early functional failures. The micron filter consisted of a pressure housing containing six 12-inch by 2-inch filter elements. A flow-through box contained pH and reference electrodes. A tap was also provided for a silt density index apparatus.

Pump Skid

The pump skid supported a Goulds multistage centrifugal pump Model 3333 size CB25-12 with 316 stainless-steel construction. Electrical requirements were 60 Hz, 230/460 volts, TEFC motor 15 horsepower at 3,600 rpm. The capacity was 18.5 gpm at 450 psi. A Mercoid pressure-sensing switch was set to shut off power to the pump should feed line pressure drop below 10 psig. Similarly, an Ashcroft high pressure-sensing switch was set to shut off power if the pressure feed to the membrane skid exceeded 400 psig. A control panel was also mounted on the pump skid. A main power switch box contained overload relays and a second box contained terminals and relays for all shutdown conditions and supplied power to the instrumentation panel. Shutdowns occurred if pH was out of range, pressure to feed pump fell below 10 psig, or discharge pressure to membranes exceeded 400 psig.

The instrumentation panel contained product electrical conductivity meter (Balsbaugh 910) and strip-chart recorder (L and N Speedomax "M" 0 to 200 µmho range) and product flow strip-chart recorder (L and N Speedomax "M" 0 to 20 gpm).

Membrane Skid

The membrane skid contained 18 cellulose acetate spiral wound elements in three pressure vessels, reject and product flowmeter, inlet and reject valves, pressure gages, and differential pressure gages.

The pressure vessel assembly consisted of the following components and characteristics:

Membrane Barrier	4" diameter
Membrane Type	Cellulose acetate
Module Dimensions	
Diameter	3.91"
Length	40"
Module Connectors	5/8" PVC couplings
Number per Pressure Vessel	6
Pressure Vessel Dimensions	
Diameter	4"
Length	20' - 11-1/2"
Pressure Vessel Material	FRP material
End Plates	PVC
Connections	
Feed	1/2" Female NPT

Reject	1/2" Female NPT
Product	3/8" Female NPT

Operating Characteristics

The following operating data was provided by the manufacturer:

Number of Elements (Total)	18
Stage One	12
Stage Two	6
Operating Temperature	70°F
Nominal Flow (gpm)	
Product	13.9 gpm
Feed	18.5
Reject	4.6
Overall Plant Conversion (Recovery)	75%
Feed Operating Pressure (Nominal)	400 psig
Salt Rejection	92.5% to 94.5%

Nominal rejection based on 2,000-ppm NaCl solution at 420 psig operating feed pressure, 10% water recovery and 77°F operating temperature.

ANALYTICAL PROCEDURES

Nitrate Analyses

Operation of all above-described apparatus and equipment for nitrate removal studies required analytical procedures and methods adaptable for field use. A further requirement was rapid analyses for nitrate monitoring during experiments on ion exchange to determine nitrate leakage and breakthrough. Ideally, continuous monitoring of process streams are most desirable for this work.

For nitrate analyses at Well 3, the HACH NI-12 test kit (range 0 to 50 mg/l N) and HACH N-14 (range 0 to 1 mg/l N) were used. The test kits, however, were not used without calibration or comparison with results obtained from State of California certified laboratories. Analyses were also performed on unknown nitrate samples supplied by the EPA laboratory in Cincinnati. HACH kit results without calibration consistently gave high nitrate results. This was determined by use of the standard additions method using certified nitrate standards and comparison with results obtained from a certified laboratory. The standard additions method was far too time consuming to be used for each nitrate analysis required. Consequently, the HACH kits were calibrated as described below.

HACH kits are supplied with numerically marked color wheels. The numbers correspond to mg/l N and are read below a pointer in the window over the color wheel. Because the pointer and graduated scale are about 5 millimeters apart, accurate readings were not possible. A hairline was glued to the window of the test kits to aid in reading the scale to 0.1 division. Several solutions were then prepared of varying nitrate concentrations from certified nitrate standards. Each solution was read on the corresponding HACH test kit with the hairline indicator and a calibration curve for each test kit was developed. Figures 14 and 15 show the accuracies of the two kits.

The NI-12 is linear in the range 0 to 12 mg/l N but consistently over 2 mg/l N too high. Considerable curvature then develops at about 15 mg/l N. The precision obtained in the region of 10 mg/l N is 10.0 + or -.4. A standard "practice" solution supplied by EPA with a concentration of 10.2 mg/l N was read as 10.2 + or -.4 using the NI-12 kit and Figure 14 as a calibration curve.

The N-14 kit gave much closer readings to the standard values as seen in Figure 15. A standard "practice" solution supplied by EPA with a concentration of 0.22 mg/l N was read as 0.22 + or -0.004 directly from the N-14 readout dial.

EPA-supplied unknowns were determined and reported as 0.710 and 6.00 mg/l N and compared by EPA to actual values of 0.700 and 6.00 mg/l N, respectively.

A quality control program was initiated in January, 1980, to compare field nitrate tests with those obtained by a certified laboratory. The results are listed in Table 2. Generally, readings obtained with the HACH kit were in excellent agreement on the processed water where, in each case, nitrate levels were less than 40 ppm. On Well 3 data, the HACH method was on the average 12 percent too low indicating that high sulfate may possibly interfere with the method.

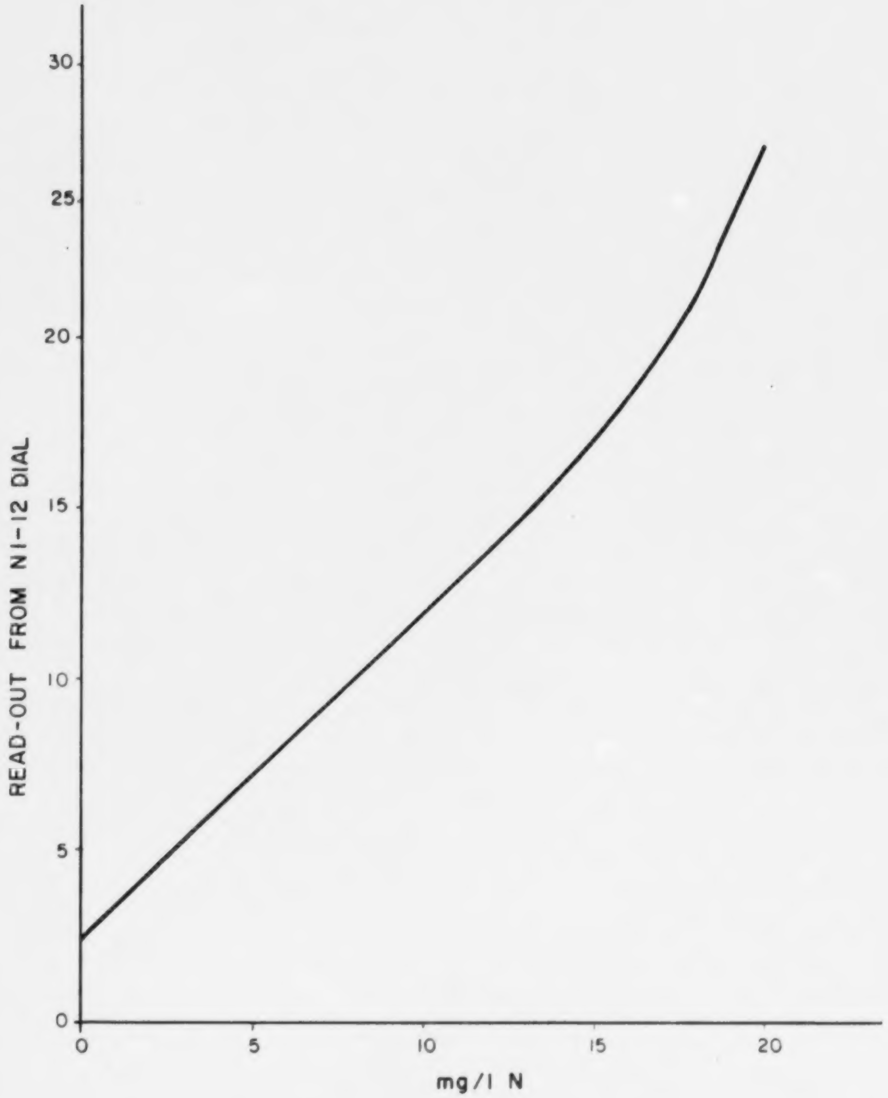


FIGURE 14 : CALIBRATION CURVE FOR HACH NI-12

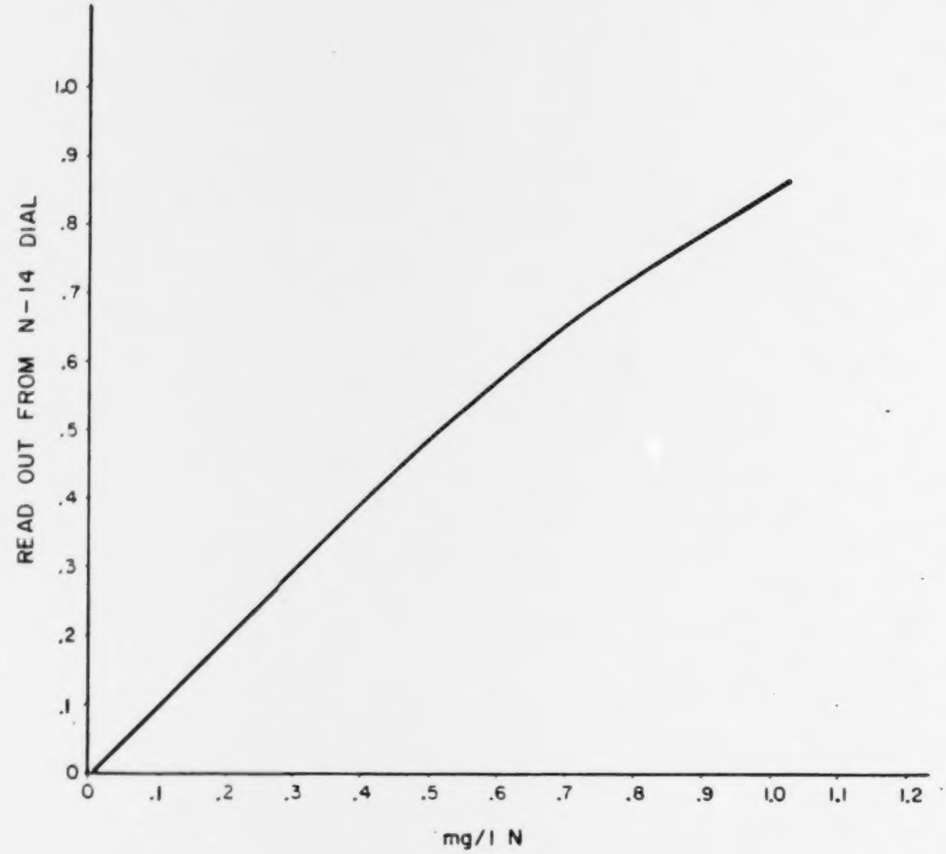


FIGURE 15 : CALIBRATION CURVE FOR HACH N-14

TABLE 2. COMPARISON OF NITRATE ANALYSES BY CERTIFIED LABORATORY AND HACH KIT METHOD

Well 3 Data		
Date	Certified Laboratory	HACH Kit
6-15-79	95.3	96.8
6-28-79	85.9	96.8
1-15-80	92.1	79.2
2-18-80	88.6	69.5
2-21-80	92.1	70.0
3-3-80	97.5	84.5
3-10-80	99.7	86.2
3-17-80	97.5	82.7
3-19-80	106.3	82.3
3-24-80	97.5	88.0
3-31-80	79.7	80.9
4-3-80	104.6	87.1
4-7-80	104.6	85.4
5-1-80	97.5	78.3
7-29-80	88.6	75.7
8-4-80	99.7	79.2
8-18-80	93.9	81.8
9-2-80	104.5	101.2
9-15-80	96.6	88
Average	95.9	83.9

Processed Water			
Date	Certified Laboratory	HACH Kit	Product From
1-15-80	20.8	20.2	R.O.
2-1-80	31.9	29.9	R.O.
5-1-80	34.6	30.8	R.O.
5-1-80	0.9	1.1	R.O.-I.X.
6-6-80	6.2	6.2	R.O.-I.X.
6-6-80	39.4	30.35	R.O.
7-29-80	42.5	39.2	R.O.
Average	24.7	21.5	R.O.

Sulfate Analyses

Sulfate analyses were performed by the turbidimetric method (APHA Standard Methods, 14th edition, 496, 1975) using HACH reagents and a HACH DR/2 spectrophotometer.

Chloride Analyses

Chloride analyses were performed by Mohr argentometric method (APHA Standard Methods, 14th edition, 303, 1975).

Bicarbonate Analyses

Bicarbonate analyses were performed by the alkalinity titration method (APHA Standard Methods, 14th edition, 278, 1975).

WATER QUALITY OF McFARLAND WELLS

Chemical Characteristics

Four wells are owned and operated by McMWCo. The wells are 800 to 1,000 feet deep and pump from a water level of approximately 250 feet.

Chemical analyses of Well 3 were obtained at frequent intervals during the course of the study. The water had been used as a domestic supply prior to mid-1978 when the study began. Consequently, production from the well was limited to the study effort. It was noted that iron deposits would frequently occur on the ion exchange columns when the pumping was limited to the experimental work. This was essentially eliminated by wasting enough water to cause the pump to cycle once per hour to prevent iron oxides from builing up on the well casing.

The water is considered to be of generally poor quality especially high in nitrate, total solids, sulfate, and hardness.

As can be seen from the analyses of Table 3, deterioration of quality occurred after domestic use stopped. Significant increases occurred over the study period in all major constituents.

A more complete record of major anions is given in Table 4. Again increases have occurred since earliest measurements with components varying independently.

A comparison of compositions of the four wells in McFarland is given in Table 5. As is seen, Well 1 is of excellent quality. Wells 2 and 4 also exceed nitrate MCL on the dates of analyses.

TABLE 3. COMPOSITION OF McFARLAND WELL 3 WATER (ppm)

Constituent	Data 5-31-78	 6-14-79	 4-3-80
Calcium	132	150	154
Magnesium	3.5	4.0	4.3
Sodium	80	88	92
Potassium		3.5	5.2
Iron	<.05	<.05	<.05
Manganese	<.01	<.01	<.01
Fluoride	.03	.06	0.11
Carbonate	0	0	0
Bicarbonate	78.8	84	88
Chloride	86.7	95.9	93.1
Sulfate	261	290	300
Nitrate, Nitrite	79.7	95.3	104.6
Arsenic	<.01	<.01	<.01
pH	8.0	7.8	7.4
Hardness (as Calcium Carbonate)	344.7	391.8	403.0
Total Solids	686	772	798
Electrical Conductivity	900	990	960
Color Units	1	1	1
Odor	None	None	None
Turbidity (NTU)	0.23	0.43	0.32

TABLE 4. RECORD OF MAJOR ANION COMPOSITION OF WELL 3

Date	Nitrate	Bicarbonate	Chloride	Sulfate	TDS
5-31-78	79.7	78.8	86.7	261	686
7-24-78	86.4	74.5	89.2	282	750
11-8-78	82.4	99.6	89.2	285	727
2-20-79	54.9	89.2	69.4	220	576
6-15-79	95.3	84.0	95.9	290	772
6-28-79	85.9	86.6	90.3	320	787
10-2-79	93.0	83.2	94.9	310	
1-15-80	92.1		91.0	340	843
2-18-80	88.6	84.9	91.0	330	
2-21-80	92.1				
3-3-80	97.5	82.5	95.9	325	
3-10-80	99.7	87.5	93.5	320	
3-17-80	97.5	90.1	92.8	330	
3-19-80	106.3	98.7	90.6	308	
3-24-80	97.5	98.7	94.5	305	
3-31-80	79.7	87.5	91.0	305	
4-3-80	104.6	88.4	93.1	300	
4-7-80	104.6	100.5	91.3	320	
5-1-80	97.5	121.3	94.2	310	827
7-29-80	88.6	78.0	93.1	310	774
8-4-80	99.7	79.7	94.2	295	
8-18-80	93.9	95.3	91.7	295	
9-2-80	104.5	108.3	98.1	295	
9-15-80	96.6	78.8	88.1	305	

TABLE 5. COMPOSITION OF McFARLAND WELL WATER (ppm)

Well No.	1	2	3	4
Date	5-8-80	4-9-80	5-1-80	4-16-80
Calcium	28	88	156	78
Sodium	50	65	100	72
Bicarbonate	88	102	121	95
Chloride	28	86	94	51
Sulfate	51	105*	310	182
Nitrate	30	67*	98	47
TDS	235	466	827	485
pH	7.7	7.2	7.3	7.7

---

*Analyses on 5-31-78 gave sulfate = 261 and nitrate = 78.

Nitrate levels have been recorded over several years of operation of these wells. Certified laboratory analyses from 1965 are shown in Figures 16, 17, 18, and 19. Well 1, the best of the four wells, shows a very high nitrate level during the 1969 to 1970 winter season and a general down trend since that time. Well 2 shows highest nitrate levels also during the winter season and lows in summer. Well 3 shows generally increasing nitrate with no levels below the standard for the past six years and only four such occurrences for the past 16 years. Well 4 shows a gradual improvement except for the last year.

Nitrate levels are known to vary seasonally with pumping frequency and duration of pumping. These fluctuations have definite implications concerning design and operation of nitrate removal facilities. Continued nitrate monitoring of wells would be of great importance to minimize operating costs of a nitrate removal plant.

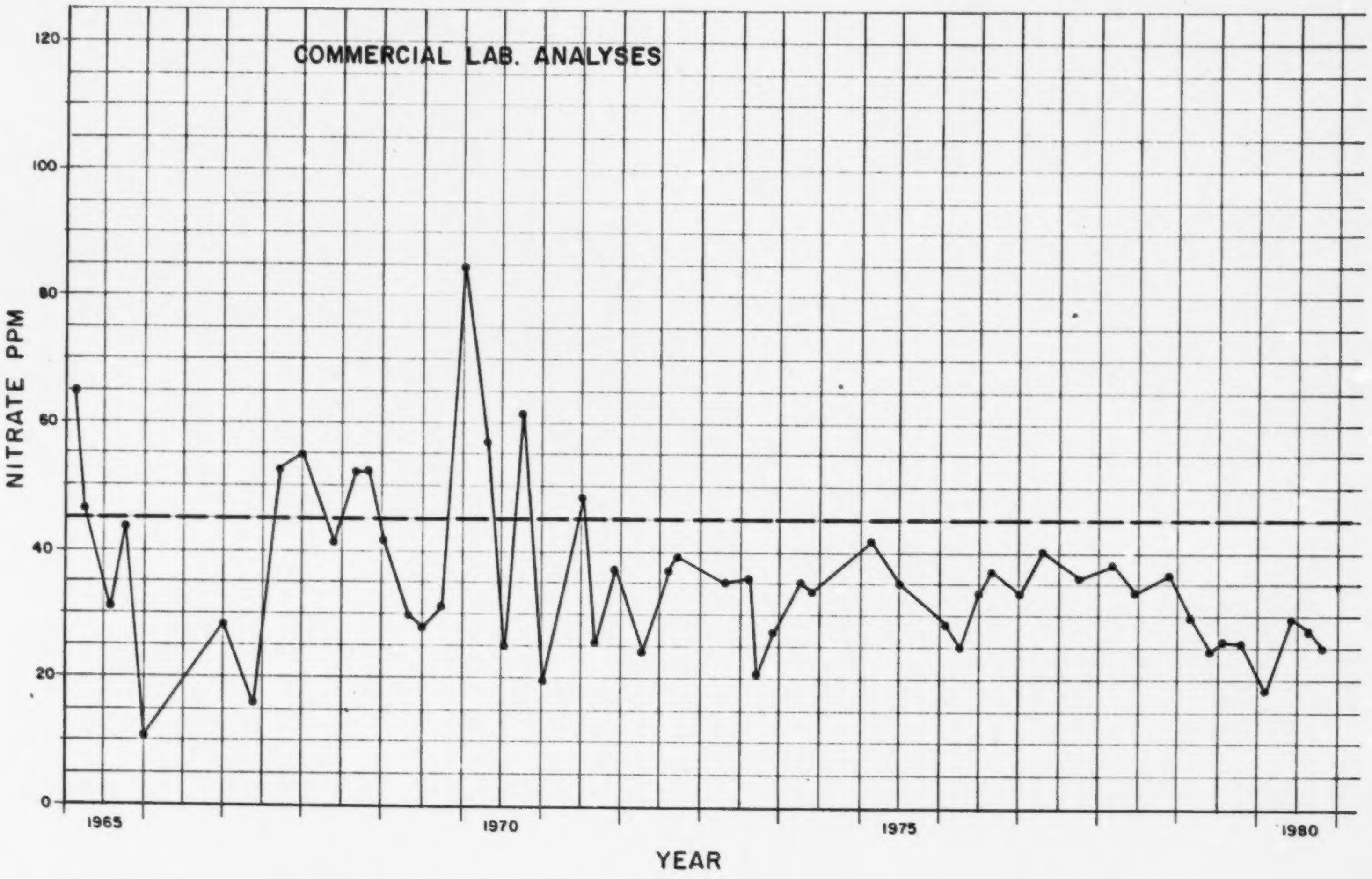


FIGURE 16 : McFARLAND M.W.CO. - WELL NO. 1

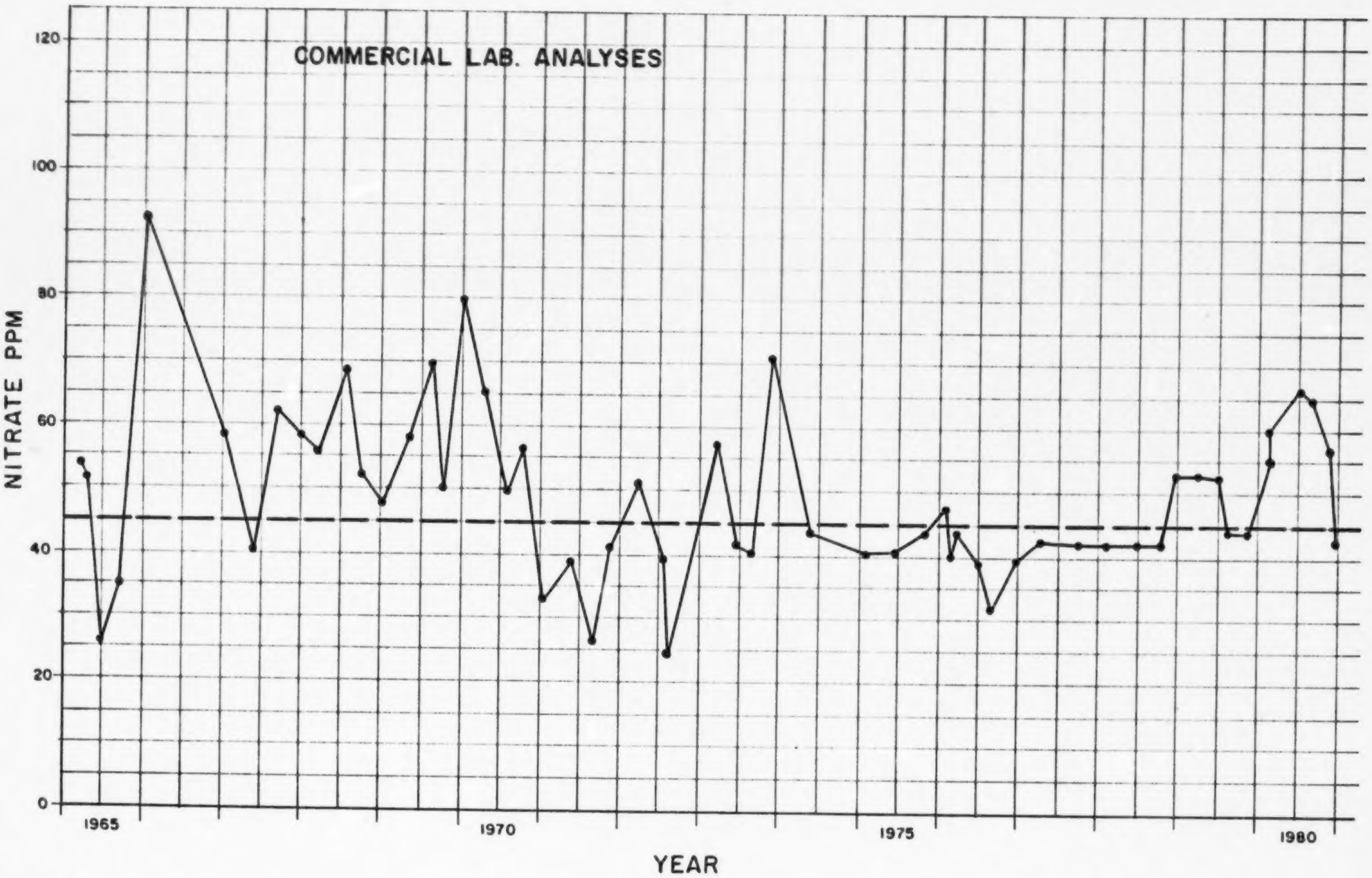


FIGURE 17 : McFARLAND M.W.CO. - WELL NO. 2

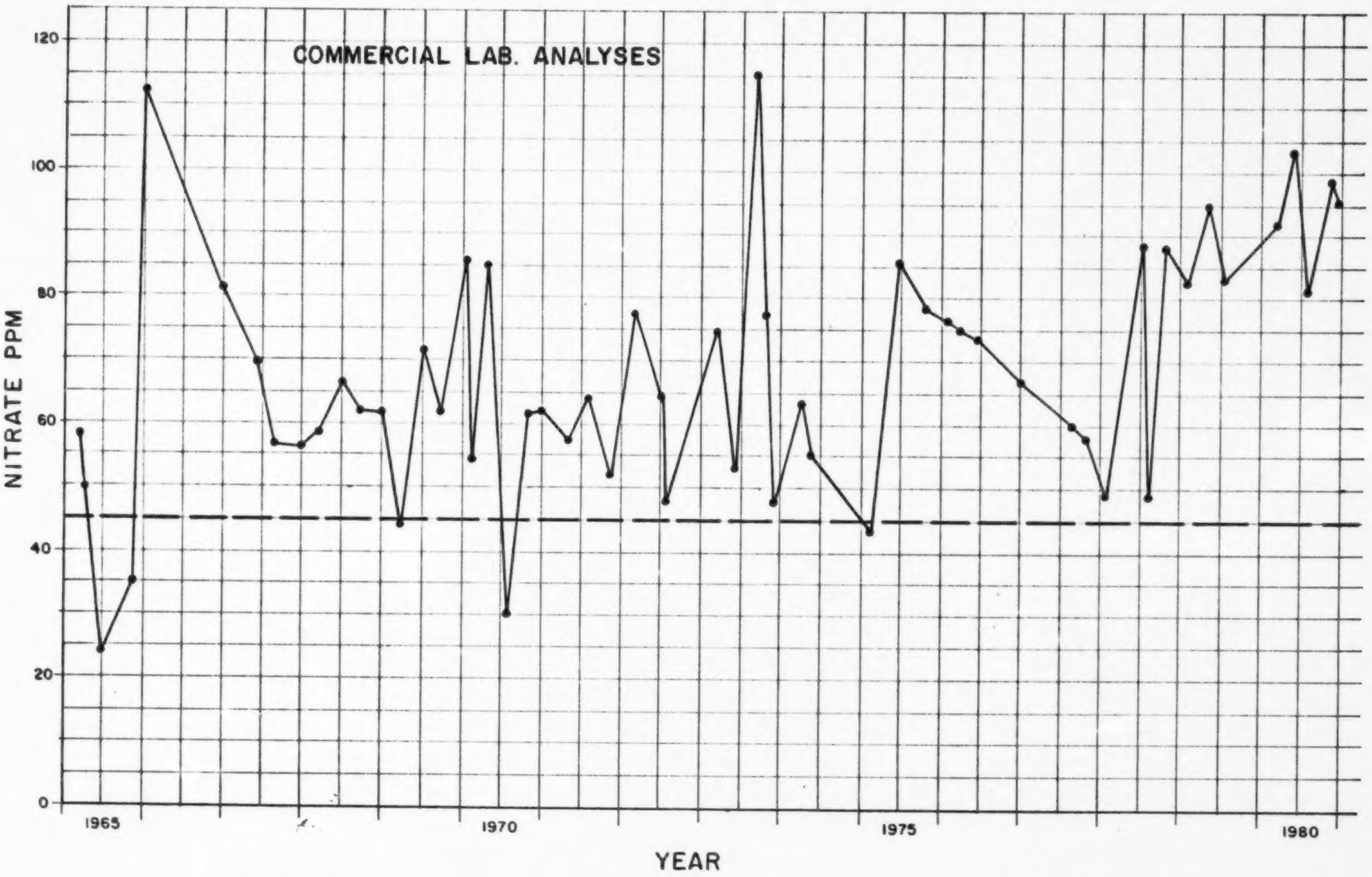


FIGURE 18 : Mc FARLAND M. W. CO. - WELL NO. 3

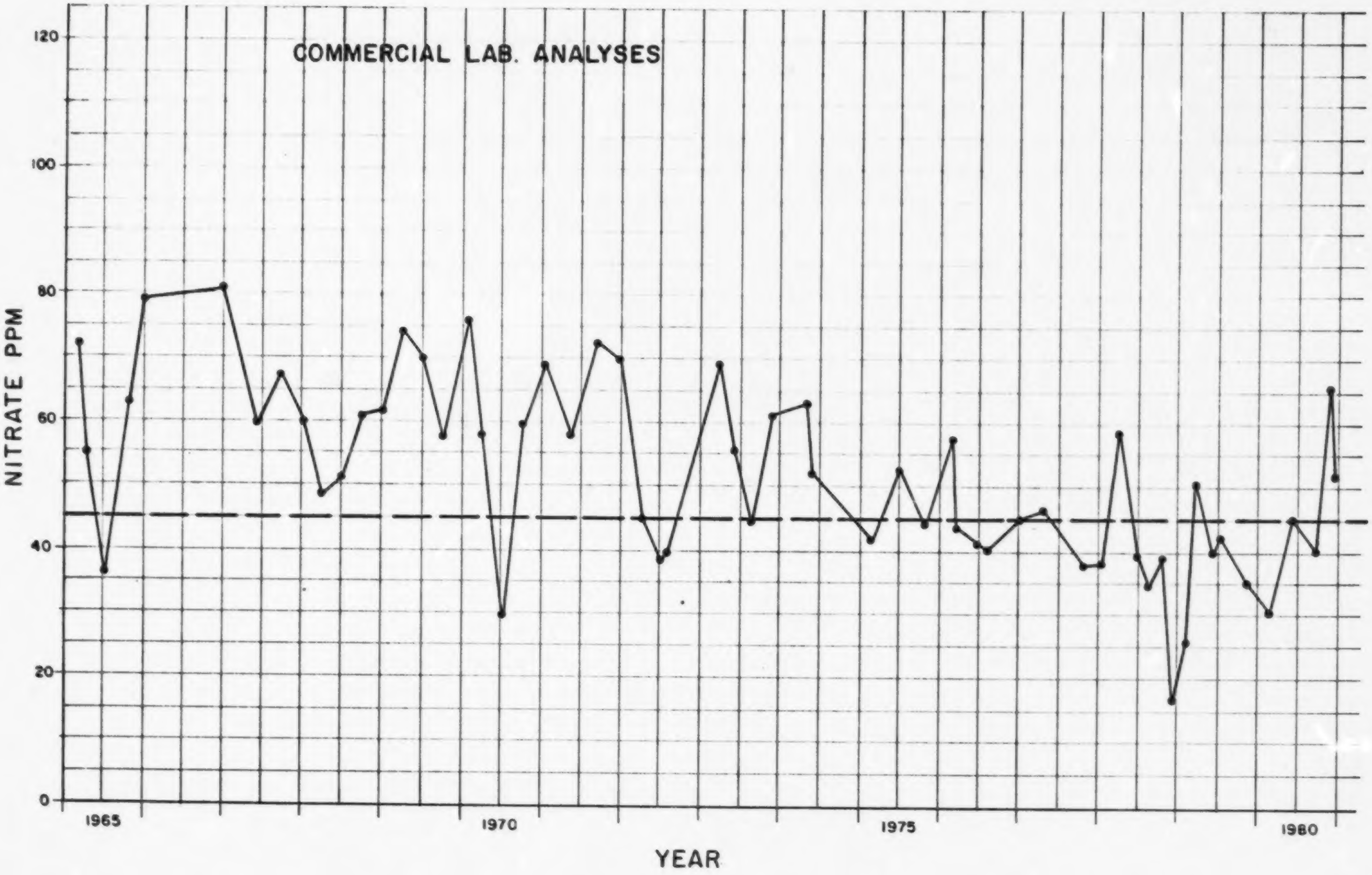


FIGURE 19 : McFARLAND M. W. CO. - WELL NO. 4

SECTION 5

RESULTS OF REVERSE OSMOSIS AND ION EXCHANGE SYSTEM OPERATION

OPERATION OF R.O. SYSTEM

The R.O. system was installed on the pad as shown in Figures 7 and 10 and operated on Well 3 water. Initially, 24-hour per day operation was maintained after the startup and checkout periods. However, after mechanical and electrical difficulties were encountered (see discussion on operational problems), operation was limited to time periods when personnel were onsite. Consequently, the system was shut down daily. Considerable downtime was also required for major repair and adjustment by servicemen. The system was operated for approximately six months until massive leakage of brine into product line occurred. A total of 1,053 hours of operating time were accumulated. Chemical analyses of Well 3 are given in the previous section.

Table 6 gives product water analyses from January through July, 1980. Table 7 gives chemical analyses of feed, product, and brine after approximately 30 days of operation of the system. Nitrate passage was approximately 35 percent with the product being essentially sodium nitrate with lesser amounts of sulfate, chloride, and bicarbonate. Chloride passage was 6.4 percent and sulfate passage was 1.3 percent. Although bicarbonate passage was high (66 percent), bicarbonate in feed was low because of pretreatment with sulfuric acid. Passage of bicarbonate as carbon dioxide can occur at low pH giving high percent bicarbonate passage. TDS passage was 7.7 percent.

TABLE 6. ANALYSES OF R.O. PRODUCT - WELL 3

	1-15-80	4-3-80	5-1-80	6-5-80	7-29-80
Calcium (Ca)	2.5	5.0	6.0		
Magnesium (Mg)	0.16	0.21	0.29		
Sodium (Na)	7.2	10	17		
Potassium (K)		0.9	0.6		
Carbonate (CO_3)		0.0	0.0		
Bicarbonate (HCO_3)		0.0	17.3	25.1	10.4
Chloride (Cl)	3.9	7.1	8.1	6.7	22.3
Sulfate (SO_4)	<5	11	<5	<5	60
Nitrate (NO_3)	20.8	39.9	34.6	39.4	42.5
Hardness as $CaCO_3$		13.4	16.2		
Total Solids @ 105°C	53	70	76	200	
pH	4.1	5.7	5.4	6.0	
Electrical Conductivity mhos/cm (K x 10^6) @ 25°C	130	120			320

TABLE 7. TREATMENT OF WELL 3 BY R.O. (2-1-80)

Constituents	Pretreated Feed	Product	Brine
Calcium (Ca)	154	7.0	590
Magnesium (Mg)	3.8	0.17	15
Sodium (Na)	92	11	345
Potassium (K)	3.6	0.5	12.8
Carbonate (CO_3)	0.0	0.0	0.0
Bicarbonate (HCO_3)	7.80	5.2	45.9
Chloride (Cl)	92.8	6.0	346.9
Sulfate (SO_4)	380	5	1,500
Nitrate (NO_3)	93.0	31.9	270.2
Fluoride (F)	0.06	0.03	0.13
Iron (Fe)	<0.05	<0.05	0.08
Manganese (Mn)	<0.01	<0.01	0.01
Arsenic (As)	<0.01	<0.01	<0.01
Copper (Cu)	<0.01	<0.01	<0.02
Zinc (Zn)	0.01	0.07	0.02
MBAS	<0.1	<0.1	0.2
Hardness as $CaCO_3$ gr/gallon 23.4	401.0	18.2	1,538
Total solids @ 105°C	823	64	3,120
pH	5.2	5.6	5.9
Electrical Conductivity mhos/cm ($K \times 10^6$) @ 25 °C	890	120	3,800

Product rate = 13.0 gpm.
Feed pressure = 390 psig.
Water Recovery = 74.3%.

Typical operating values and nitrate removal data are given in Tables 8 and 9 for over 1,000 hours of operation.

Brine pressure was normally held to less than 400 psi at the inlet to the first stage. Pressure drop across the first stage ranged from an initial 25 psi at a brine flow of 4.6 gpm to a final 40 psi at a brine flow of 4.0 gpm. Pressure drop across the second stage ranged from an initial of 25 psi and a final of 23 at the above flow rates. These data indicate a pressure buildup within the brine channels over the 1,053 hours especially within the first stage. Inspection of first stage pressure vessel interiors showed accumulation of sand, grit, and foreign matter resembling particles of the prefilter material. No excessive iron oxide was noted. Product flow was initially 12.9 gpm at a brine pressure of 390 psi. Final product flow after 1,053 hours of operation was 11.0 gpm at comparable brine flow rates and brine pressures. This represents an approximate

15 percent loss in productive capacity over this period of operation.

TABLE 8. TYPICAL OPERATION OF R.O. SYSTEM ON WELL 3

P2*, pressure at high pressure pump inlet	11 psi
P3, pressure at high pressure pump outlet	390 psi
P4, brine pressure, first stage inlet	390 psi
P5, product pressure	26 psi
DP1, pressure drop across first stage	30 psi
DP2, pressure drop across second stage	22 psi
F1, flow rate of brine	4.6 gpm
F2, flow rate of product	13.8 gpm
Percent conversion of feed to product	75%
pH of feed	5.0
Pressure drop across prefilters	2 psi
Chlorine in feed	<1 ppm

---

*See Figures 11, 12, and 13.

Table 9 summarizes data and performance of the system for nitrate removal up to 1,053 hours of operation. It is noted that nitrate passage was rarely below 25 percent and during the initial 500 hours of operation ranged between 23 and 41 percent. During the second 500 hours of operation, nitrate passage rose to over 50 percent bringing product water above the 45-ppm nitrate MCL. It was apparent that massive leakage or membrane failure had occurred at 1,028 hours of operation. Product salinity probes and first stage inspection of the system revealed first stage header-to-membrane element seals had deteriorated and would no longer retain the O-rings in position in the first stage headers. Repair of this failure required replacement of all header and element interconnectors in the first stage with interconnectors having double O-ring seals (four per connector). After these modifications, it appeared that nitrate removal was restored to normal.

Ion Exchange Polishing of R.O. Product

As shown above, nitrate removal by R.O. ranged between 25 and 50 percent over an extended period of operation. It was proposed that polishing of the R.O. product could be accomplished by anion exchange to provide a water low in nitrate and TDS which would be blendable with untreated water. The

TABLE 9. R.O. TREATMENT OF WELL 3

Hours of Operation	Date	Brine Pressure	% Product Recovery	Product (ppm) TDS	Product (ppm) Nitrate	Well 3 Nitrate (ppm)	% Nitrate Passage
100	2-12-80	390	73.7	50	22.9	67.3	34
121	2-14-80	400	74.4	47	25.2	75.7	33
133	2-18-80	390	74.3	55	22.9	69.5	33
166	2-20-80	380	73.9	50	26.0	70.0	37
244	3-21-80	357	75.4	60	21.6	84.9	25
290	4-30-80	410	77.1	48	18.0	79.2	23
310	5-1-80	370	73.3	78	18.0	78.3	23
311	5-1-80	360	73.3	70	30.8	78.3	39
394	5-20-80	385	72.8	68	28.6	74.8	38
400	5-20-80	380	73.3	70	30.4	74.8	41
415	5-21-80	380	75.0	68	22.0	79.2	28
425	5-21-80	380	71.0	65	22.0	74.8	29
440	5-22-80	380	71.0	63	21.1	74.8	28
464	5-23-80	390	71.0	60	24.6	77.0	32
490	5-24-80	390	72.7	60	13.6	69.5	20
500	5-25-80	380	71.9	58	16.3	69.5	23
535	5-26-80	390	71.0	60	22.4	72.6	31
551	5-29-80	380	71.0	65	26.0	83.6	31
617	6-7-80	380	71.3	62	30.4	79.2	38
641	6-8-80	390	71.0	73	34.8	82.7	42
654	6-10-80	400	71.0	70	43.1	82.7	52
662	6-11-80	390	75.0	73	46.2	81.8	56
692	6-13-80	400	75.0	65	22.4	82.3	27
720	6-16-80	370	71.0	80	34.8	79.2	44
731	6-17-80	380	70	65	31.2	78.7	40
757	6-19-80	390	74.2	65	30.0	79.2	38
791	6-24-80	390	73.3	65	33.0	80.5	41
850	7-1-80	370	73.3	90	35.6	81.8	44
870	7-3-80	380	74.2	65	15.8	80.5	20
882	7-8-80	380	73.3	80	12.8	80.5	16
892	7-9-80	390	74.2	65	35.6	80.5	44
925	7-11-80	400	73.3	65	33.4	79.2	42
950	7-16-80	400	73.3	70	35.6	79.2	45
978	7-18-80	390	73.3	75	16.3	79.2	21
1003	7-23-80	390	73.7	68	40.0	78.3	51
1026	7-28-80	380	73.3	75	33.4	74.8	45
1028	7-28-80	380	73.3	>100	46.6	74.8	62
1032	7-28-80	360	73.3	>100	59.0	74.8	78
1037	7-28-80	350	73.3	>100	48.8	74.8	65
1049	7-29-80	350	73.5	>100	46.5	75.7	61
1053	7-29-80	360	73.3	>100	34.8	75.7	46

average composition of the R.O. product was approximately as follows:

	ppm	meq/l
Nitrate	30	0.48
Sulfate	15	0.10
Chloride	10	0.28
Bicarbonate (as CO_2)		1.60
Total Anion		2.46

Because of the acid condition of the R.O. feed, it is assumed here that most bicarbonate from the feedwater passes into the R.O. product as carbon dioxide which is removed by the anion exchange resin as bicarbonate. From this composition, the number of bed volumes treatable to nitrate removal can be estimated for a strong-base anion exchange resin from Equation (13) (Reference 1). For a resin having an exchange capacity of 1.3 eq/l, a BV(N) of 1,317 bed volumes is estimated. If the carbon dioxide is removed prior to entering the ion exchanger, this could extend BV(N) to 2,018 bed volumes. Consequently, a bed life of 1,317 to 2,018 bed volumes could be expected.

Breakthrough curves for various levels of regeneration are given in Figures 20 through 24. Results of these tests are summarized in Table 10 and shown graphically in Figure 25. Average R.O. product nitrate levels varied from 24 to 33 ppm in these experiments. At the maximum regenerant loading, 1,500 bed volumes of product water were obtained at very low nitrate levels. It thus appears that the carbon dioxide in the product was effective in reducing the bed life by a significant amount.

TABLE 10. TREATMENT OF R.O. PRODUCT BY ION EXCHANGE

Nitrate (ppm)				
Well 3	R.O. Product (average)	I.X. Product (average)	Pounds Regenerant per Cubic Foot Resin	BV(N) Observed
75	24	2.7	45	1,500
75	27	3.0	19.5	1,400
81	33	4.3	4.6	1,100
81	30	5.1	4.6	1,150
80	32	7.9	2.3	800

Use of regenerant loading above approximately 5.0 pounds per cubic foot of resin cannot be justified. Increasing salt loading by a factor or nine increases bed life from 1,150 to

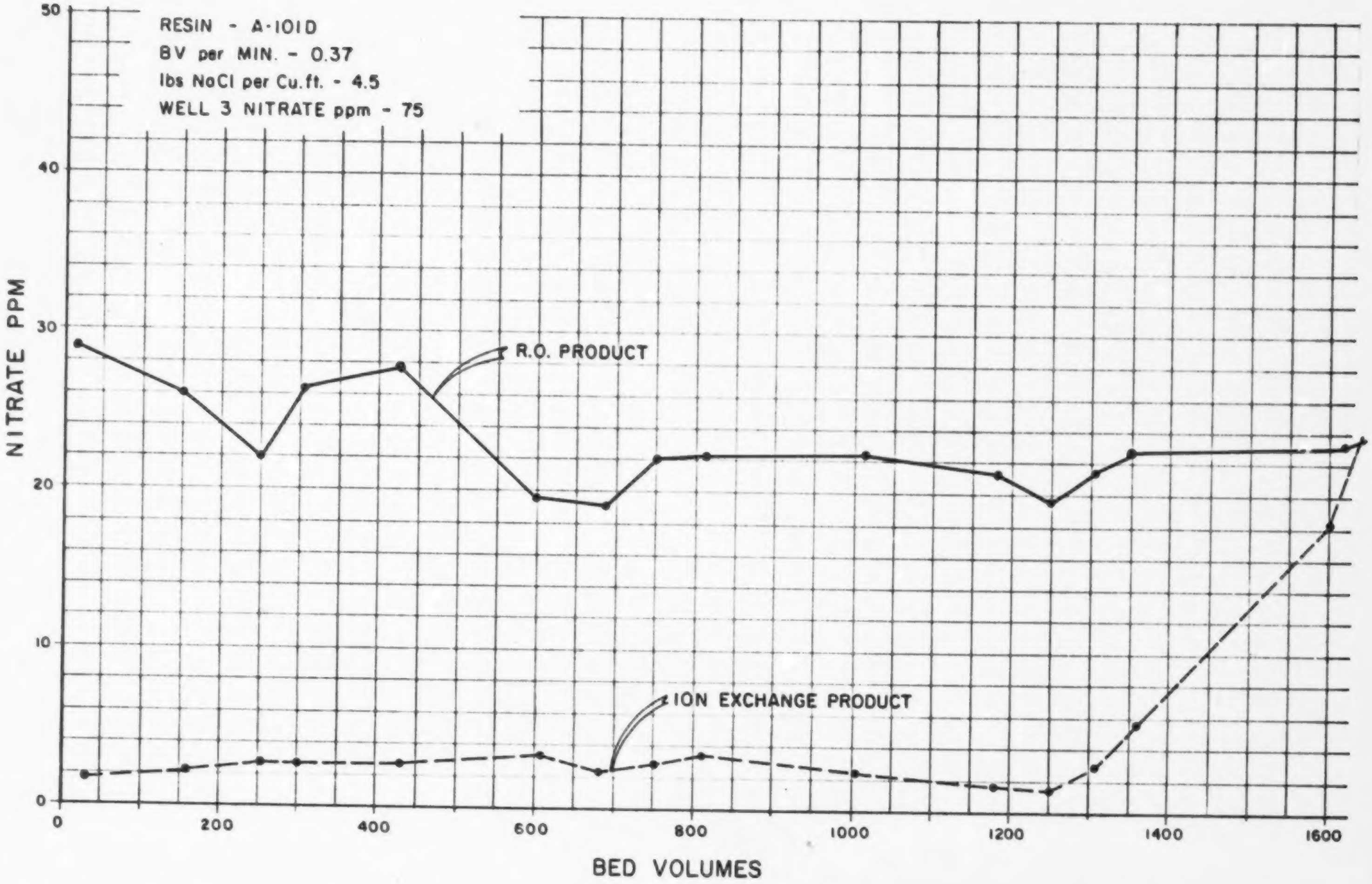


FIGURE 20 : ION EXCHANGE TREATMENT OF R.O. PRODUCT (5-20-80)

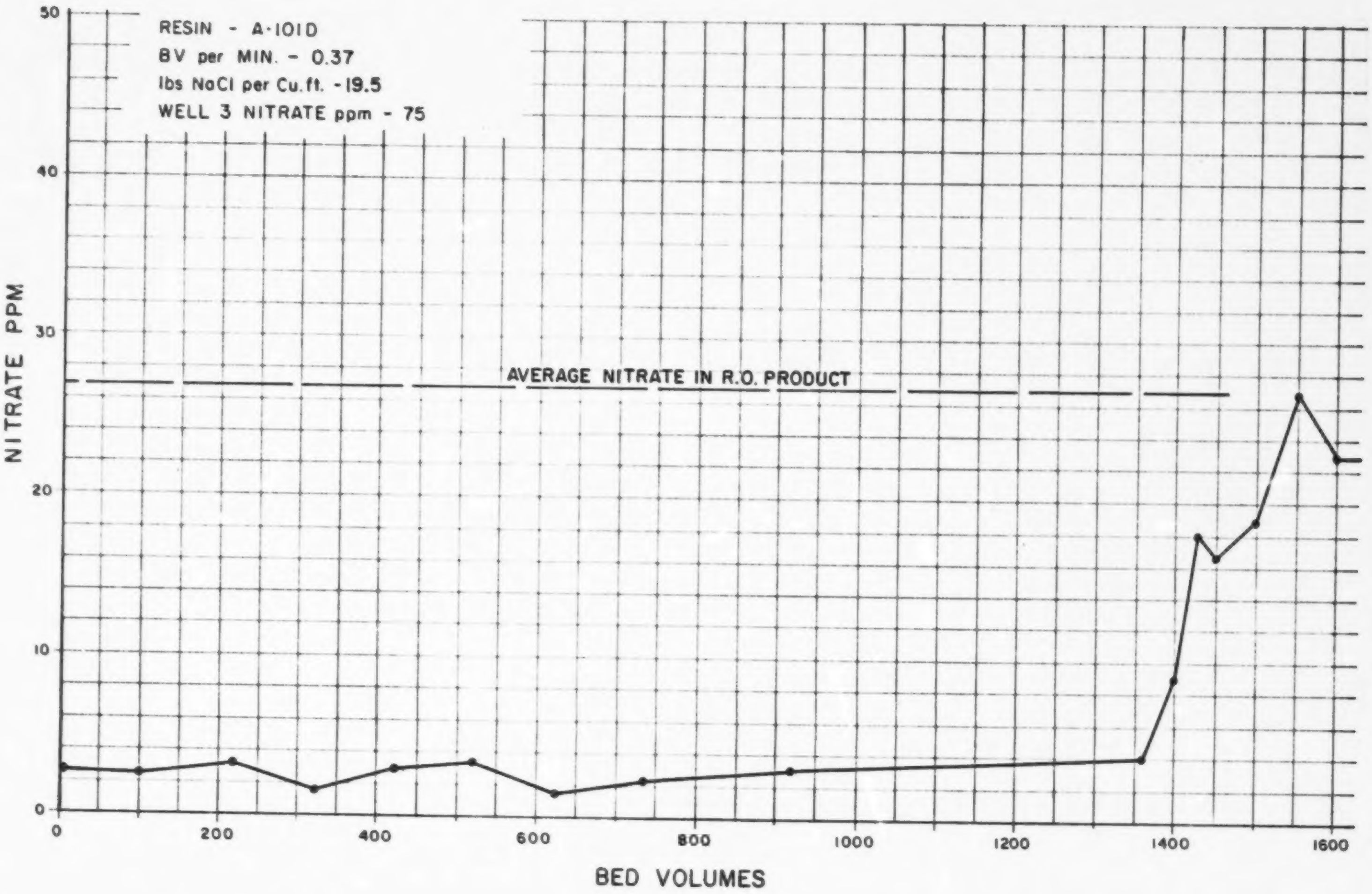


FIGURE 21 : ION EXCHANGE TREATMENT OF R.O. PRODUCT (5-23-80)

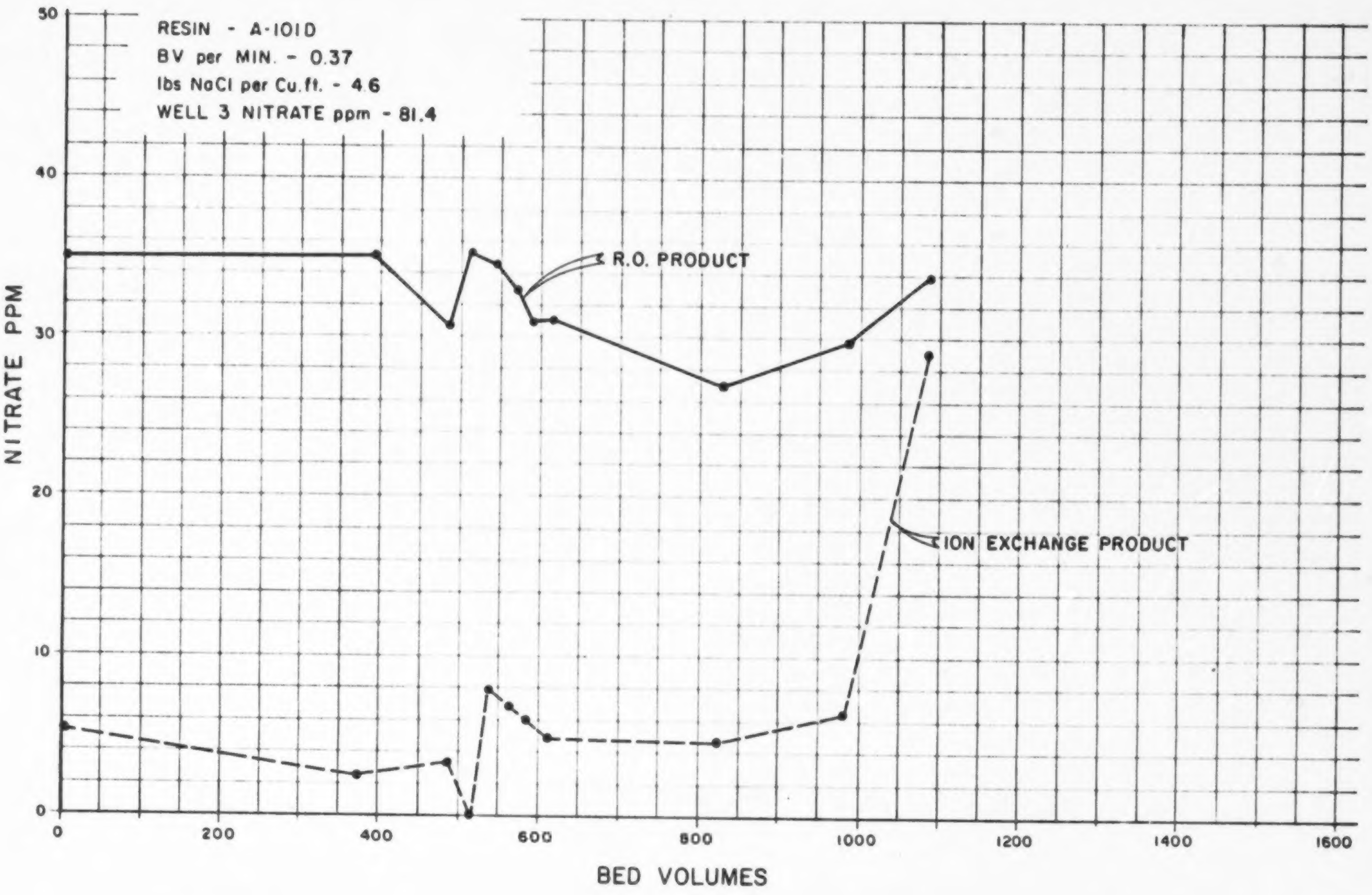


FIGURE 22 : ION EXCHANGE TREATMENT OF R.O. PRODUCT (6-3-80)

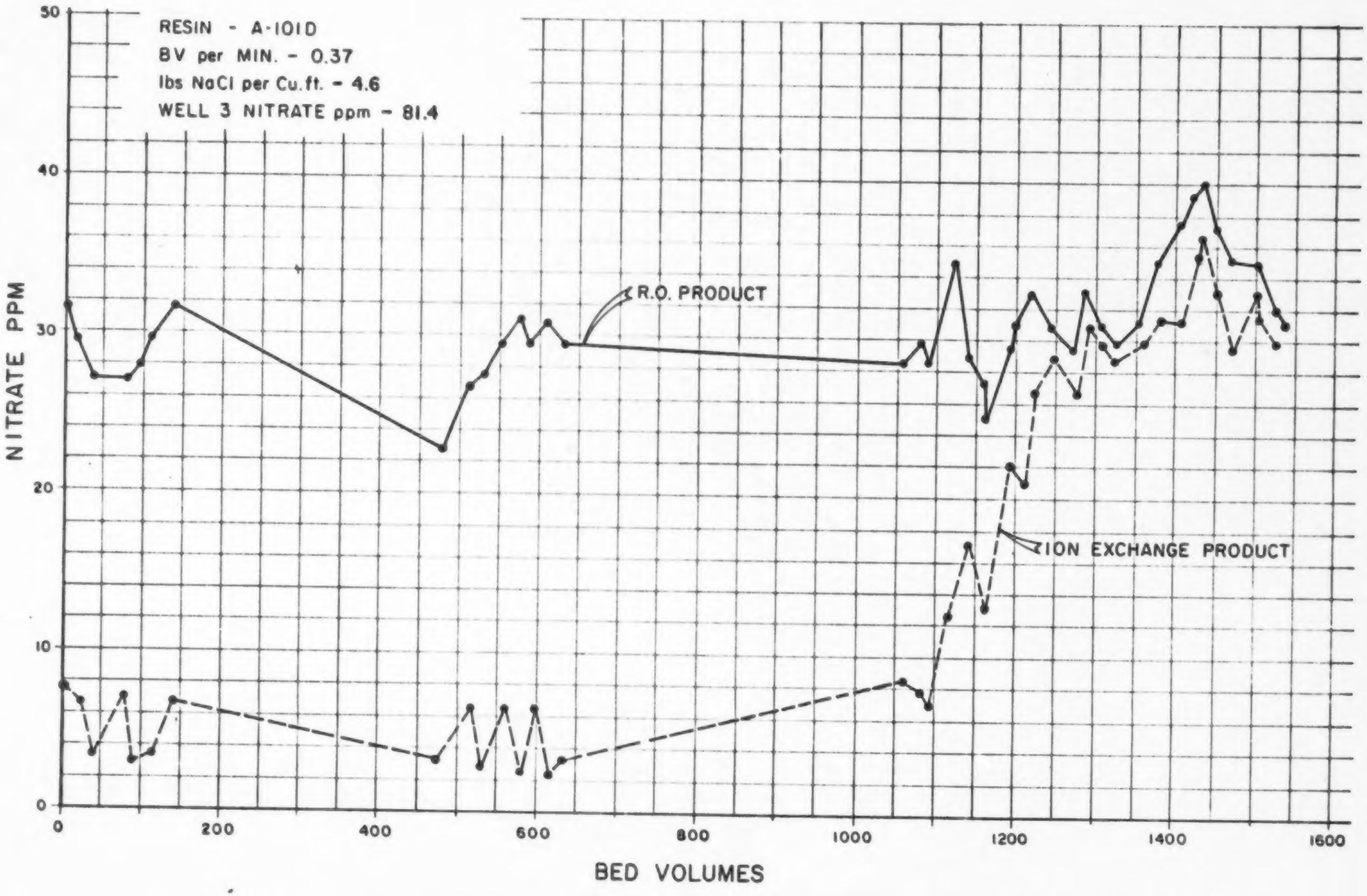


FIGURE 23 : ION EXCHANGE TREATMENT OF R.O. PRODUCT (6-12-80)

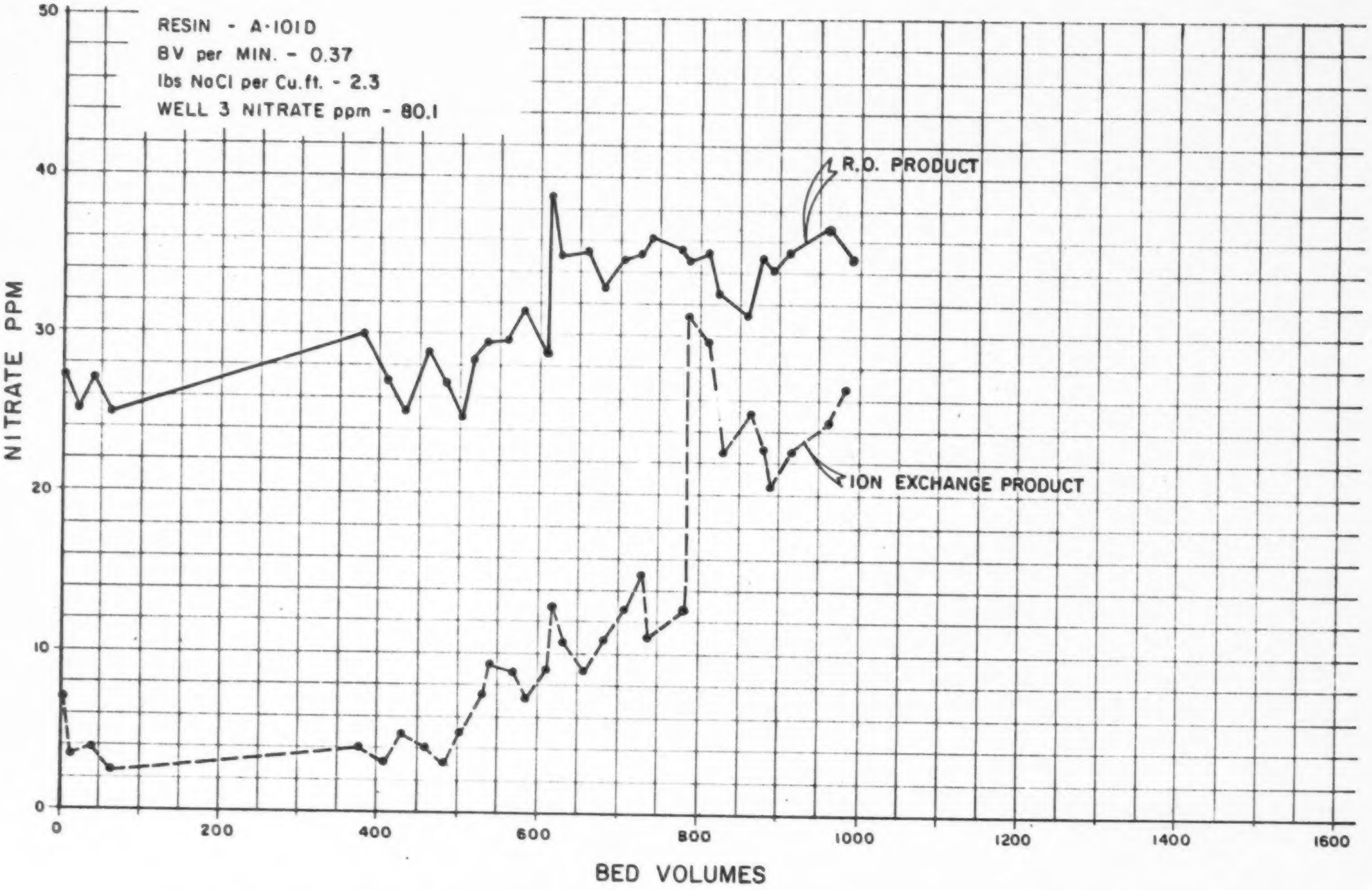


FIGURE 24 : ION EXCHANGE TREATMENT OF R.O. PRODUCT (6-18-80)

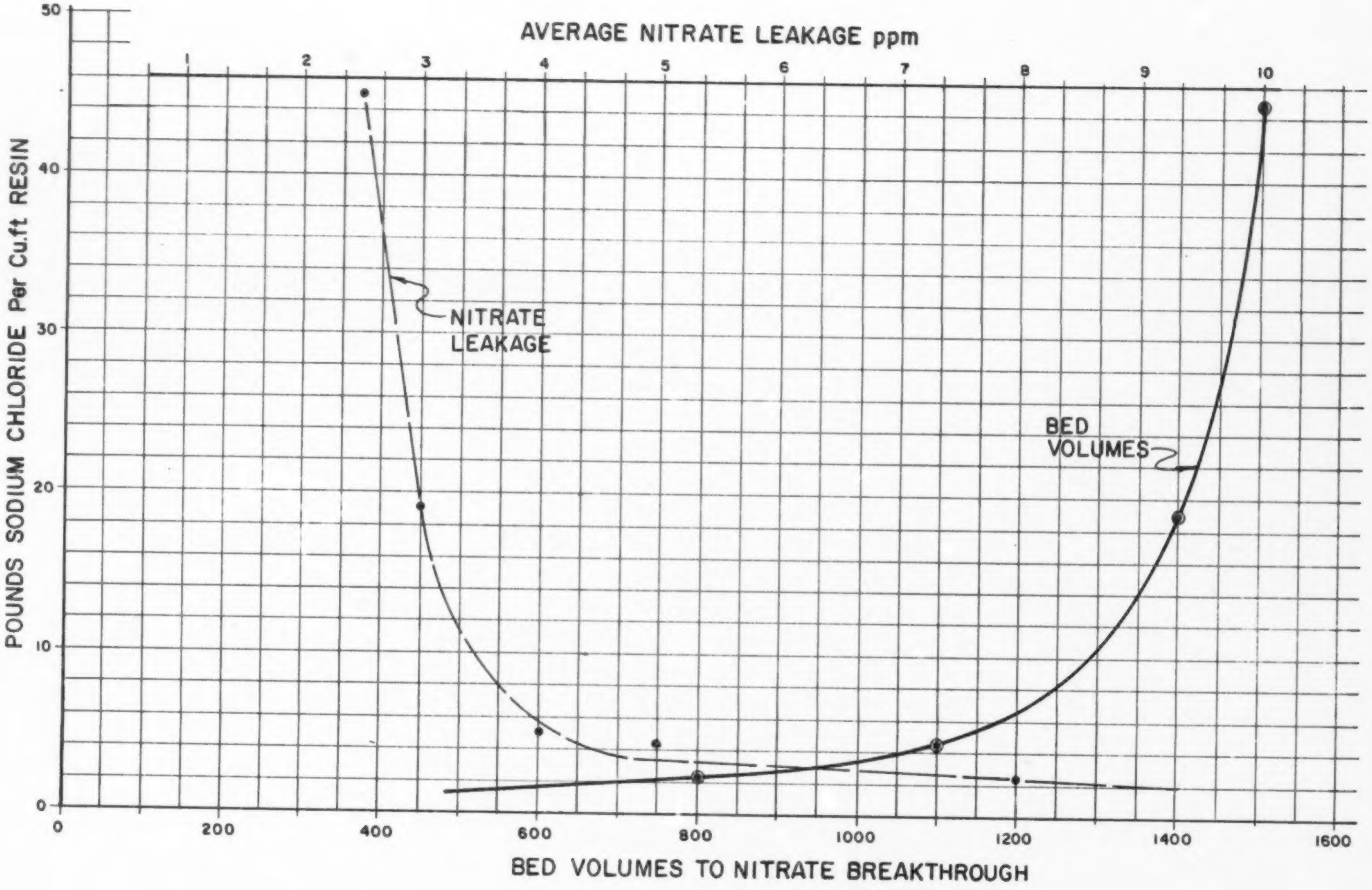


FIGURE 25 : ION EXCHANGE TREATMENT OF R.O. PRODUCT - EFFECT OF REGENERANT LOADING

1,500 bed volumes or a factor of 1.3; whereas nitrate leakage which is already low is only decreased by approximately one-half.

The values of the bed life and nitrate leakage can be estimated by those principles and equations given in Reference 1.

At the end of the run, the column composition can be estimated from influent composition and Equation 13 of Reference 1. The amount of nitrate remaining on the column after partial regeneration can be estimated from Figure A-14 of Reference 1. The nitrate leakage can be estimated using Equation 2 of Reference 1. The bed life, BV(N)' is estimated as described in Reference 1. The estimates are given in Table 11. A comparison of estimated and observed value is given in Table 12.

TABLE 11. ESTIMATION OF NITRATE LEAKAGE, BV(N), AND BV(N)' FOR POLISHING R.O. PRODUCT BY ION EXCHANGE

R.O. Product Composition (meq/l)				(1)	(2)	Regeneration Level (pounds per cubic foot)	(3) XN	(4) XN After Regeneration	Nitrate Leakage (5)	
Nitrate	Sulfate	Chloride	Bicarbonate	BV(N)	BV(N)'		End of Run		XN	ppm
0.39	0.1	0.28	1.6	1,583	1,583	45	0.48	0	0	0
0.43	0.1	0.28	1.6	1,397	1,397	19.5	0.46	0	0	0
0.53	0.1	0.28	1.6	1,247	1,119	4.6	0.51	0.15	.038	5.9
0.48	0.1	0.28	1.6	1,370	1,119	4.6	0.51	0.15	.038	5.9
0.52	0.1	0.28	1.6	1,260	882	2.3	0.50	0.30	.097	15.0

---

(1) From Equation 13, Reference 1, for fully regenerated column.

(2) From Step 3, Appendix page A-31.

(3) $$X_N = \frac{(\text{Nitrate meq/l}) \times BV(N)}{1{,}300}$$

(4) From Figure 14, Reference 1.

(5) From Equation 2, Reference 1.

TABLE 12. ESTIMATES OF PARAMETERS FOR TREATING R.O. PRODUCT BY ION EXCHANGE COMPARED TO OBSERVED VALUES

Regenerant Level lbs/C.F.	BV(N)'		Nitrate Leakage (ppm)	
	Estimated	Observed	Estimated	Observed
	1,583	1,500	0	2.7
19.5	1,397	1,400	0	3.0
4.6	1,119	1,100	6	4.3
4.6	1,119	1,150	6	5.1
2.3	882	800	15	7.9

The estimates compare favorably with the observed pilot column tests.

Ion Exchange Polishing of R.O. Product - Use of R.O. Brine as Regenerant

From the above results obtained by treating Well 3 water with R.O., it is seen that the sulfate-to-nitrate ratio in the brine is 6.7 (31 meq to 4.6 meq). This is greater than that found in the R.O. product which has a corresponding ratio of 0.2 (0.1 meq to 0.5 meq). As a consequence, the sulfate-to-nitrate ratio on the resin at the end of the run after treating the R.O. product water can be raised significantly if the resin is then treated with the R.O. waste brine. Because sulfate is generally more easily removed from the resin by sodium chloride than nitrate, there may be some advantage to doing this. The corresponding mole fractions of resin in the sulfate or nitrate form can be estimated in each case.

If a column is operated on the R.O. product, $\overline{X_N}$ at the end of the run is approximately 0.48 (see Table 11). By treating the column with an R.O. brine, the resin in the sulfate form can be estimated from Equation 4 of Reference 1 using brine composition given in Table 7.

$$\frac{\overline{X_s}}{(1 - \overline{X_s})^2} = K_N^s \frac{\overline{c}}{c} \frac{X_s}{(1 - X_s)^2}$$

$K_N^s = 0.04$

$\overline{c} = 1,300$ meq/l

$c = 45$

$X_s = 0.69$

$$\frac{\overline{X_s}}{(1 - \overline{X_s})^2} = \frac{0.04 \times 1,300}{45} \quad \frac{0.69}{(1 - 0.69)^2} = 8.3$$

$$\overline{X_s} = 0.70$$

The mole fraction of resin in monovalent ion form will be 0.30. Because of the presence of chloride in the R.O. brine, the amount of nonsulfate or monovalent resin in the nitrate form, X'_N, is estimated from Equation 2 of Reference 1.

$$\frac{\overline{X'_N}}{1 - \overline{X'_N}} = 4 \times \frac{.29}{1 - .29} = 1.63$$

$$\overline{X'_N} = 0.62$$

The fraction of the resin in the nitrate form will then be 0.30 x 0.62 or 0.186.

Consequently, treatment of the resin by the R.O. brine will reduce the nitrate fraction of the resin from $\overline{X_N} = 0.48$ to $\overline{X_N} = 0.186$ or by 0.29 x 1,300 = 377 meq of nitrate per liter of resin. Regeneration of the resin by sodium chloride will be required to remove the sulfate and further reduce the nitrate if enough is used. Because the resin contains 70 percent sulfate, 3.4 pounds of sodium chloride per cubic foot of resin will be required to remove it. The bed life will be 1,289 bed volumes and nitrate leakage would be 7.9 ppm. Comparing these estimates with the curves of Figure 25, it is seen that at 3.4 pounds of regenerant a leakage of 6-ppm nitrate and a bed life of 1,025 bed volumes can be expected without any treatment by R.O. brine. Consequently, on this basis, the bed life could theoretically be extended by approximately 25 percent by using the R.O. brine as a partial regenerant.

Experiments were conducted by treating the resin bed of the 20-inch pilot column with the R.O. brine after the resin bed was exhausted with R.O. product. An example of the effluent profile is shown in Figure 26. It is seen that nitrate removal from the column is considerable for the first 25 bed volumes as sulfate is absorbed on the column. Nitrate removal continues to approximately 100 bed volumes. The amount of nitrate removed from the column up to 100 bed volumes is estimated from this curve as 450 meq of nitrate per liter of resin; this is comparable to the above estimate of 377 meq of nitrate from theoretical considerations.

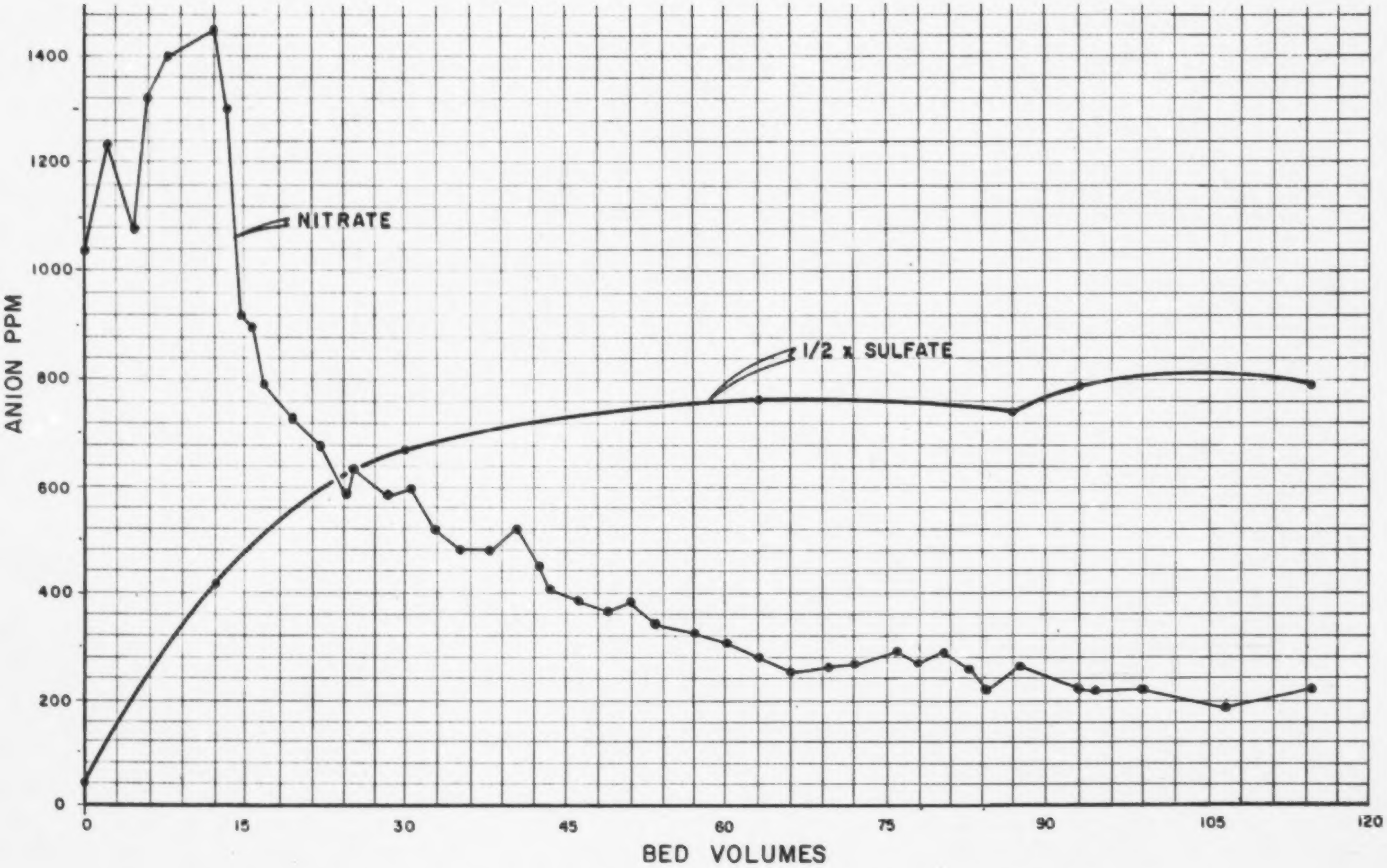


FIGURE 26 : TREATMENT OF SPENT RESIN WITH R.O. BRINE

Subsequent treatment of the resin by sodium chloride regenerant will remove the sulfate and some nitrate. In a typical run, the resin was treated with 4.6 pounds of sodium chloride per cubic foot of resin. As developed above, 3.4 pounds are required for sulfate removal. The extra 1.2 pounds will reduce nitrate from $\overline{X}_N = 0.19$ to $\overline{X}_N = 0.13$. From this and a feed composition (nitrate = .56, chloride = .28, bicarbonate = 1.60, sulfate = 0.10) using Equation 14 (Reference 1), life for such a column is estimated to be 1,132 BV(N) with a nitrate leakage of approximately 6 ppm.

Unfortunately, only one complete run was made before final R.O. system breakdown. The effluent curve is shown in Figure 27 for polishing the R.O. product of the above R.O. product composition. BV(N) is approximately 1,200 bed volumes with an average nitrate leakage of approximately 2.5-ppm nitrate. Had the column been regenerated without treatment with the R.O. brine and only using 4.6 pounds of regenerant per cubic foot of resin $\overline{X}_N$ would be reduced from $\overline{X}_N = 0.48$ to 0.15 (from Figure A-14, Reference 1).

This would give a bed life of 1,107 BV(N) and a leakage of about 7-ppm nitrate, compared to a BV(N) of 1,200 and leakage of 2.5 as was actually obtained. Thus giving an extended bed life of 8 percent higher than use of chloride brine alone would give and a significantly lower leakage. It is noted that Figure 27 shows not only low leakage of nitrate but also considerable leakage of sulfate. Apparently, the sodium chloride brine was not effective in removing the high sulfate loads from the column and removed more nitrate than expected. This unexpected and unexplained effect is certainly favorable.

The above observation that pretreatment of the column with R.O. brine was not effective in extending bed life by any significant extent is explainable. In the region of $\overline{X}_N = 0.5$, the slope of Curve A, Figure A-14, Reference 1, is quite steep indicating that chloride brine is as effective in removing nitrate (approximately 1 eq per 1 eq) as it is in removing sulfate; consequently, there is little or no advantage to replace nitrate with sulfate in those cases where $\overline{X}_N$ is near or greater than 0.5. In other words pretreatment by R.O. brine followed by a chloride brine does not remove significantly more nitrate than treatment by brine alone.

The use of the R.O. brine as a pretreatment for regeneration would be most useful for more fully nitrate loaded columns and where low nitrate leakages are desirable. For example, if carbon dioxide is removed from the R.O. product, the composition would be approximately:

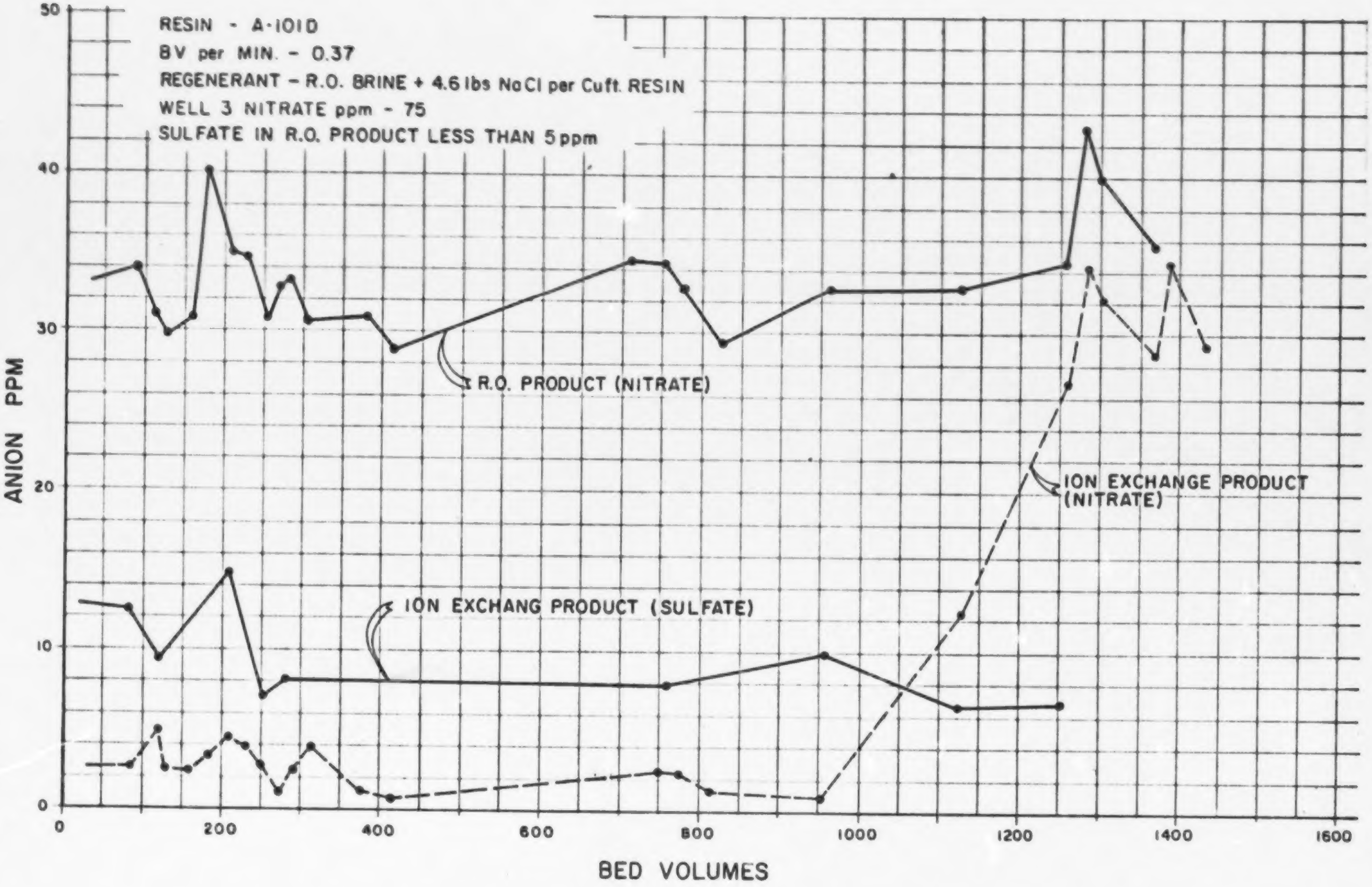


FIGURE 27 : ION EXCHANGE TREATMENT OF R.O. PRODUCT AFTER REGENERATING RESIN WITH R.O. BRINE AND SODIUM CHLORIDE

TABLE 13. COMPOSITION OF R.O. PRODUCT

Nitrate	0.39 meq/l
Sulfate	0.10
Chloride	0.28
Total Anion	0.77

The resin would have an $\overline{X_N}$ value of approximately 0.760 after treatment of 2,535 bed volumes to nitrate breakthrough. To bring such a column to $\overline{X_N}$ = 0.15 for a leakage of 2.0-ppm nitrate, approximately 6.7 pounds of sodium chloride regenerant per pound of resin is required. Pretreatment by the R.O. brine would reduce the brine demand to 4.6 pounds or a redution of 31 percent in brine usage could be realized.

Test Results With Single-Module R.O. System - Membrane Comparison Tests

The single-module R.O. system described in Section 4 of this report provided the capability to test nitrate removal for five different membrane elements. These elements are also described above. These tests were intended primarily to select a membrane for use in the pilot plant R.O. system for nitrate removal studies reported above. The characteristics sought were high nitrate-to-sulfate ratios in the R.O. product. This would provide a product for efficient nitrate removal by anion exchange polishing since the interference by sulfate would be minimum. This would also provide a brine with a higher sulfate-to-nitrate ratio with potential use as a regenerant for the anion exchange polisher.

Feedwater from Well 3 was treated with sulfuric acid to adjust the pH to 4.1. The water was not chlorinated. Each R.O. module was operated in the single-module R.O. loop system for one to two hours before data was taken. Data on nitrate and sulfate removal are given in Table 14. The best overall performance was obtained with the DuPont B-9 module giving high water recovery. The membranes giving the highest nitrate-to-sulfate ratio, however, were the spiral wound high pressure operated cellulose acetate membrane and the Dowex hollow fiber membrane operating at 200 psi.

A series of tests were also conducted using the Dowex element to determine if the nitrate to sulfate ratio of the R.O. product could be increased by operating at lower pressures.

The data are given in Table 15. The nitrate-to-sulfate ratio in the product droped to 2.5 at 40 psi. These data

TABLE 14. COMPARISON OF R.O. MEMBRANE TYPES ON McFARLAND WELL 3 WATER

Membrane		% Water Recovery Per Single Module	Feed Pressure	Product (ppm)			Brine (ppm)		
I.D.	Type			NO_3	SO_4	TDS=	NO_3	SO_4	TDS=
PA-300	SP[a]	34	400	20.2	21	75	145.2	455	925
CA-HP[b]	SP[a]	24	395	32.6	2	50	132.0	480	900
CA-LP[c]	SP[a]	17	200	77.4	44	255	112.6	445	825
Dowex R.O. 25	HF[d]	4.5	200	26.4	4	50	110.0	400	780
DuPont B-9	HF[d]	52	310	8.8	2	25	189.2	600	1,175

---

[a] SP = Spiral wound.
[b] CA-HP = Cellulose acetate high pressure.
[c] CA-LP = Cellulose acetate low pressure.
[d] HF = Hollow fiber.

Feedwater composition ppm:

NO_3^- = 105.6; Cl^2 = 0

SO_4 = 365

TDS= = 750

pH = 4.1

[=] TDS = Measured by R.O. meter

indicate relatively poorer nitrate removal at higher pressures when compared to sulfate.

TABLE 15. DOWEX R.O.25 PERFORMANCE ON WELL 3

Feed Pressure (psig)	Product Nitrate (ppm)	% Nitrate Removal	Product Sulfate (ppm)	% Sulfate Removal	Equivalent Ratio of Nitrate to Sulfate
170	26.1	75.8	4	98.9	5.1
125	31.8	70.5	4	98.9	6.1
80	46.7	56.7	8	97.8	4.5
40	66.6	38.2	21	94.3	2.5

Brine Flow Rate = 0.7 gpm
Feed Nitrate = 107.8 ppm
Feed Sulfate = 367.5 ppm

Operational Problems With R.O. System

The pilot R.O. system described in Section 4 of this report was installed with all piping, electrical, and instrumentation controls. Membranes were installed according to vendors instructions.

From the time of initial system checkout and startup, serious operational problems occurred. These difficulties cause concern for the reliability of using an R.O. system at a remote well site.

In small community water systems, such as McFarland's, little maintenance personnel can be available for a complex system. Furthermore, any system of well site treatment must be capable of intermittent operation to coincide with well pump on-off cycling or adequate storage must be provided. Experience gained on this program does not favor the use of R.O. for well site treatment.

Failure of High Pressure Seals. Before high pressure was applied to the system, low pressure tests (30 to 50 psi) were made to check the hydraulics and low pressure nitrate removal and demineralization capabilities.

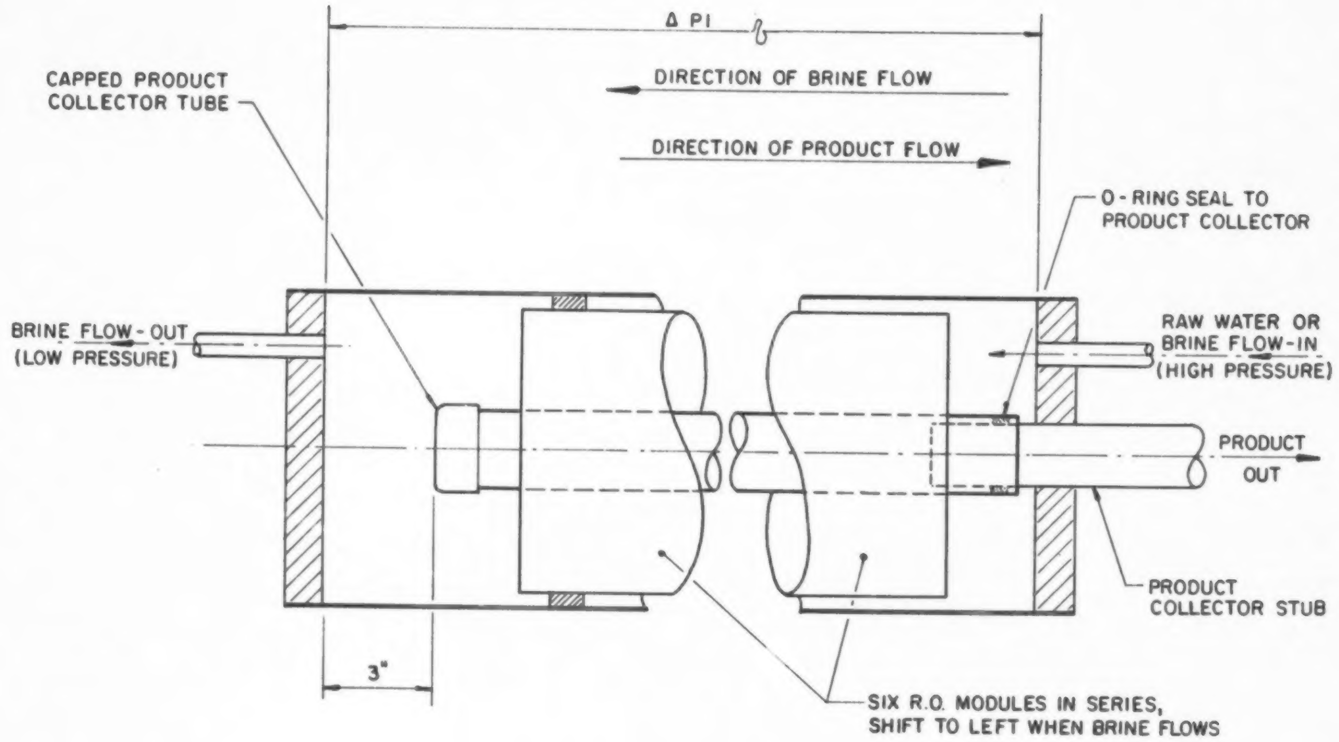
Hydraulic testing of the system failed when low water pressure was applied. The hydraulic failure was caused by pressure opening the seals within the pressure vessels causing direct leakage of the brine stream into the product channels.

This can best be described with reference to Figure 13 showing the external hydraulic flow pattern and Figure 28 showing internal flow and the membrane element-to-header connector of the first stage. Shortly after a slight hydraulic pressure was applied to the system, a pressure drop, ΔP1, developed across the membrane modules causing them to shift approximately 3 inches toward the low brine pressure end (to the left in Figure 28) thus breaking the seal between the product collector tube of the first element and the header which contained a product collector stub (exact design of stub is not shown). Because the flow pattern and type of element interconnectors were design details which were left to the option of the manufacturer, the vendor was immediately notified of this problem. A manufacturer's representative installed 3-inch spacers inside the pressure vessels at the low pressure end to prevent movement of the elements.

Operation with this modification continued for over 1,000 hours until the O-ring seal to the product collector would no longer hold an O-ring in place during high pressure operation. This was apparently due to wear caused by the slight lateral back-and-forth movement of the elements as the system was turned on and shut off on a daily basis. The vendor was again notified of this failure. Element-to-element seals and element-to-header seals were then replaced with seals having double O-rings. The previously used 3-inch spacer was no longer needed since the new type connectors filled the entire length of the pressure vessel.

It is believed that the opposite flows of brine and product was a fundamental cause of the above failure in the first stage. It should be noted that in the second stage, brine and product flows are in the same direction--toward the control panel as shown in Figure 28. No failure of high pressure seals was experienced in this stage. Had first stage product flow been in the same direction as brine flow (i.e., both to the left in Figure 28), the product would exit in the left header and the element-to-header seal would be subjected to less lateral movement and hence less wear during low to high to low pressure excursions. With opposite flows, this seal must withstand the movement of all elements, whereas with parallel flows each element can absorb some movement. Because nitrate rejection by the membranes was not as good as other anions, it is necessary to maintain the high pressure seals as tight as possible. In other applications, such as simple demineralization of brackish water, these seals may not be as critical.

Brine Flow Regulation. After the hydraulic leakage was corrected as described above, high pressure was applied to the system. Brine flow and pressure were regulated as per manufacturer's instructions by brine discharge Valve V4 and brine Regulators V1, V2, and V3. See Figures 12 and 13. It was not possible to sustain a low enough brine flow without causing ΔP1 and ΔP2 to be excessive (above 40 psi). The vendor was



Δ PI
DIRECTION OF BRINE FLOW
DIRECTION OF PRODUCT FLOW
CAPPED PRODUCT COLLECTOR TUBE
O-RING SEAL TO PRODUCT COLLECTOR
BRINE FLOW-OUT (LOW PRESSURE)
RAW WATER OR BRINE FLOW-IN (HIGH PRESSURE)
PRODUCT OUT
PRODUCT COLLECTOR STUB
3"
SIX R.O. MODULES IN SERIES, SHIFT TO LEFT WHEN BRINE FLOWS

FIGURE 28 : CAUSE OF HYDRAULIC FAILURE IN R.O. PILOT PLANT

again informed. A field engineer found a plumbing irregularity in the brine feed system causing the high pressure cutoff switch to reflect brine pressure on the booster pump side of V2 rather than on the side of the membrane skid. Thus, it was not possible to restrict brine flow using V2 to a low enough value and to give ΔP1 and ΔP2 of 25 psi without the pressure regulator cutting power to the booster pump. Plumbing alterations were required to correct the situation.

Minor Operational Problems. During the period of system operation, relatively minor electrical and mechanical problems were encountered. System shutdown began to occur with no apparent reason. Conference with the manufacturer's service department were ineffective in locating the problem. This required a third service call to find a faulty overload relay adjustment within the power control box. Chemical feed pumps required replacement of check valves and other internal pump parts which were chemically attacked by the concentrated acid and hypochlorite feed solutions. These pumps also required continuous adjustments to keep chlorine and pH within safe levels of operation. Although a pH detector and power controller functioned well, manual acid feed adjustment was still required to prevent the automatic pH detector-power controller from frequently cutting power to the system. Automatic level controls of the chemical feed system failed early in the test and were disconnected.

Prefilters required replacement approximately every 150 hours of operation. Although iron content of Well 3 was less than 0.05 ppm, sand and grit mixed with iron oxides was found to accumulate on the prefilters. It is possible this material has accumulated in the hydropneumatic tank over a period of one to two years.

The use of hexametaphosphate additive was not necessary since precipitation of calcium salts within the system was not likely. If this were necessary, an additional maintenance would be required to replenish the hexametaphosphate every three days according to manufacturer's recommendations. Maintenance for membrane cleaning was not required during the operation of the system although one cleaning cycle was performed. This required approximately eight man-hours for this system.

SECTION 6

RESULTS OF ION EXCHANGE PILOT COLUMN TESTS

Ion exchange pilot column tests were extensively reported in Reference 1. A few additional ion exchange tests were run with the pilot column loaded with A-101D using Well 3 water to test performance at higher flow rates and measure resin performance loss.

CONTINUATION OF FLOW RATE STUDIES

Previous tests were made using flow rates up to 1.38 BV/minute at 22.5 gpm per square foot bed area without loss of nitrate removal efficiency. These tests were continued to 2.75 BV/min or 45 gpm per square foot bed area and gave no indication of decreased efficiency. Tests at this higher rate using 4.58 pounds of sodium chloride regenerant per cubic foot of resin gave a leakage of 20-ppm nitrate to a BV(N) of 100. This compares to performance reported in Table 12 of Reference 1.

Pressure drop through the system at the highest hydraulic load including the inlet and outlet hydraulic valves, flow distributor and collector, inlet screen, and 24 inches of resin bed was 22 psi. This is considerably higher than the pressure drop across the bed of 20 to 50 mesh resin. The system used was designed for much lower flow rates of about 5 gpm per square foot. Pressure drop across the resin bed alone should be about 4 psi per foot of bed depth at the 45 gpm per square foot loading.

CHANGES IN RESIN CAPACITY

After one year of nitrate removal service in the pilot column, samples of the A-101D resin were returned to the manufacturer for evaluation together with samples of unused resin. The salt splitting capacities (equivalents per liter) were reported as 1.26 (fresh) and 1.28 (used). Sphericities were reported as 98 and 99. The report noted that the used sample "was in excellent condition, displaying chemical and physical characteristics comparable to new resin."

After 18 months of service in the pilot column, a sample was removed and placed in a 2-inch laboratory column, fully regenerated with sodium chloride, and exhausted with Well 3 water. A parallel test was made with fresh A-101D. This test showed a loss of 13 percent in nitrate removal capacity. The used resin had a definite iron oxide coloration.

SECTION 7

COST ESTIMATES FOR SINGLE-BED ION EXCHANGE SYSTEM

CONCEPTUAL DESIGN

The conceptual design of a single-bed ion exchange plant shown in Figure 29 is based on use of phased twin beds. By "single-bed" is meant passage of the water to be treated through an ion exchange bed (contained in one or more vessels) composed of one resin type until the exchange resin is exhausted. The bed is then removed from service and regenerated with sodium chloride brine in downflow mode. During regeneration of the bed, a second ion exchange bed is put into service. Operation can be either in the complete or partial regeneration mode.

The primary equipment required are resin tanks equipped with flow distributors for introduction of raw water and removal of backwash water. A second flow distributor should be installed to introduce regeneration brine near the upper surface of the resin bed. A filter system at the bottom of the resin tank supports the resin and collects the treated water. Tanks for storage of salt and brine are also required.

Brine can either be pumped or educted from the brine tank, mixed with untreated water, and allowed to pass through the brine distributor through the resin and then to waste. Brine is passed downflow through the resin.

After exhaustion of the anion exchange resin, nitrate will be concentrated at the bottom of the column due to chromatographic separation of sulfate and nitrate. In downflow regeneration, the nitrate is thus ideally closest to the exit end of the column and need not be moved by the regenerant through the entire bed. After regeneration, any nitrate remaining on the column will also be concentrated at the base of the column. This will require declassification (mixing to form a homogeneous resin composition throughout the column) of the resin before it is put back into service. Because of these characteristics, the service cycle should be followed by brine rinse and then backwashing and/or declassification.

Column operation is easily automated making labor requirements minimal. The regeneration cycle can be initiated

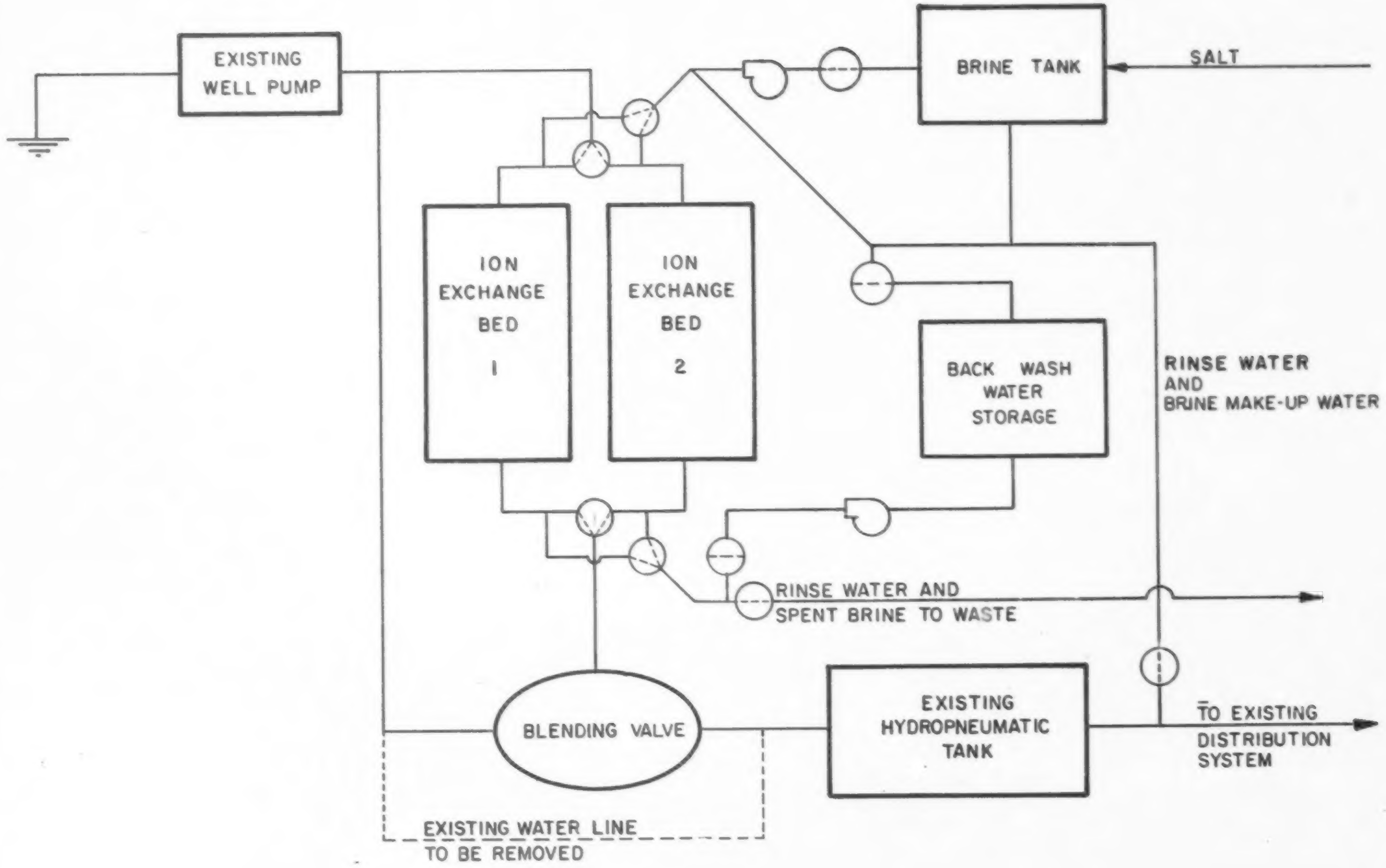

EXISTING WELL PUMP
ION EXCHANGE BED 1
ION EXCHANGE BED 2
BRINE TANK
SALT
BACK WASH WATER STORAGE
RINSE WATER AND BRINE MAKE-UP WATER
RINSE WATER AND SPENT BRINE TO WASTE
BLENDING VALVE
EXISTING HYDROPNEUMATIC TANK
TO EXISTING DISTRIBUTION SYSTEM
EXISTING WATER LINE TO BE REMOVED

FIGURE 29 SINGLE BED ION EXCHANGE CONCEPTUAL DESIGN

by an integrating flowmeter on the treated water stream. Ideally, continuous nitrate monitoring with automatic alarm and control system should be employed. The backwash and regeneration periods are controlled by a single timer which controls the flow of processing water through the system's values.

The design is based on the concept of retrofitting existing well site facilities (well pump and hydropneumatic tank) as are presently in use in the McFarland, California, area. A blending valve is provided for use when only a portion of the well supply is treated. Refinements in a detailed design could include out-of-phase operation to allow the latter portion of one bed's service cycle to be blended with the initial portion of the second bed's service cycle. This may be required to level out the alkalinity of the treated water and reduce corrosivity. Another refinement can be introduced by separating spent brine and brine rinse streams if alternative methods of brine disposal are available; one for concentrated waste and one for dilute waste. Although upflow (counterflow) regeneration can be used, special equipment and operating techniques are required. The costs and production parameters are estimated below using conventional downflow regeneration.

SIZING OF CONVENTIONAL SINGLE-BED ION EXCHANGE SYSTEM

The beds are sized to treat water pumped directly from a well through the ion exchange columns into a surge tank serving the municipal water system.

Resin Quantity - Tank Size

Well water production rate (mgd)	1.0
(gpm)	694
Fraction of well water treated by ion exchange	1.0
Volume to be exchanged (gpm) (avg)	694
at maximum pump rate (gpm)	907
Minimum volume of resin on stream at 20 gpm/square foot; 36-inch bed depth; 6.67 gpm/cubic foot (cubic feet)	136
Tank size diameter (inches)	91.2
height (inches)	60
Use two available tanks diameter (inches)	72
height (inches)	60
Resin volume, cubic feet per bed	169

Operational Factors

Brine requirements for treatment of a water having the composition of McFarland Well 2 are estimated by the method described in Reference 1.

The McMWCo Well 2 has the following approximate composition:

NO_3^-	= 56.7 ppm	= 0.91 meq/l
HCO_3^-	= 71.9	= 1.18
Cl^-	= 60.5	= 1.70
$SO_4^=$	= 197	= 4.10
	Total Anion	= 7.89

Use of the method described in Reference 1 to estimate the amount of regenerant to reduce nitrate at Well 2 to 30 ppm gives the following values:

NO_3^- leakage (ppm)	= 30
Salt loading (pounds/cubic foot)	= 3.71
Bed volumes treated	= 199
Salt requirement per 1,000 gallons Well 2 water treated (pounds)	= 2.49
Salt requirement per 1,000 gallons blended (50/50) water (pounds)	= 1.25

Other operating parameters are estimated as follows:

Treated water NO_3^- level (ppm)	= 30
Estimated bed capacity (BV)	= 199
Per cycle (gallons)	= 251,560
Time for exhaustion at (minutes)	= 362
average flow rate (hours)	= 6.04

*Brine rinse at 1.0 BV of 6% NaCl, min (gallons) = 15 (1,264)

*Slow rinse 3.5 BV, min (gallons) = 45 (4,424)

*Backwash 5 gpm per square foot resin area (recyclable), min (gallons) = 10 (2,827)

Time for regeneration cycle (min) = 70

Wastewater gallons per cycle = 5,688
BV = 4.5
gpd = 22,601

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*Per cycle.

Reduction of nitrate to 30 ppm would provide a water suitable for blending with an equal portion of raw water having a nitrate level below 60 ppm. If 50/50 blending is done, water is treated at one-half the rate estimated above, i.e., at 10 gpm per square foot of bed area. This reduces wastewater to 2,844 gallons per cycle or 11,300 gpd at the average flow rate of 1 mgd.

Although the beds are sized for treatment of 100 percent of well capacity, blending would not utilize the full capacity. However, historical trends show increases in nitrate and sulfate; consequently, oversizing would allow 100 percent treatment to continue into the future.

COST OF ION EXCHANGE FACILITY

Equipment Costs for 1-mgd Production

The following estimates are based on the conceptual design of Figure 29. Prices are derived from vendors' quoted prices of commercially available ion exchange equipment. A single bed of resin is employed using a pair of 72-inch-diameter resin tanks containing a total of 136 cubic feet of resin. Proper flow distribution is important. A second pair of resin tanks is included to allow continuous operation; one bed being in service while the second bed is being regenerated and washed. The system does not include automatic nitrate analyses but does include a continuous sampler which can provide for one test per day of nitrate level of product water. Cycling is controlled by manual setting of flow integration. These costs are representative of an installation at McFarland, California, where weather conditions do not require a facilities building and where property area is adequate at the well site.

The required equipment is:

4	Fabricated resin tanks 72" x 60" (including valves, electrical controls, and flow distributors)	$71,600
1	Backwash storage tank and pump	5,000
	Accessories, reset meters, brine pump, air injector	8,500
1	40-ton brine maker (including level controls sight glasses)	18,000
338	Cubic feet resin at $150 per cubic foot	50,700
	Pad, installation, and startup	5,000
	TOTAL	$158,800

Specific Well Supply System Applications

The above equipment costs can increase or decrease for a specific well supplied water distribution system. If buildings, instrumentation, automatic controls, hydropneumatic tank, prefiltration, iron removal, and land area are required, further capital investments must be made.

Decreased costs can be realized if less than 100 percent usage of a single well can be permitted. The system shown in Figure 29 has a 6.04 hour service period and a 1.17 hour regeneration period, and each resin bed is used 50 percent of the time. If only one bed is used, the well could be in service for 84 percent of a 24-hour period. This would reduce equipment costs from $158,800 to $97,650. Such a system would be particularly suitable if two nearby wells were equipped and operated in a synchronous or staggered mode to continuously supply the distribution system with 1.68 times the capacity of one well and each resin bed could be in service 84 percent of the time. Costs could further be reduced by $18,000 if a single brine supply system could be utilized by two nearby existing wells. Added cost for a brine line would be required.

Amortized and Operating Costs per Quantity of Product Water

The operating costs are derived for the system shown in Figure 29 operating treating 1 mgd of Well 2 water in McFarland, California, without blending. The costs listed in Table 16 are given in cents per various water quantities.

TABLE 16. OPERATING COST ESTIMATE FOR ION EXCHANGE FACILITIES

			Cost per Unit Quantity of Water Treated (c) ($)		
		Annual Costs	Per 1,000 Gallons	Per Cubic Meter	Per A-F
Equipment and Installation Cost (see above)	$158,800				
Engineering (Design and Lab Testing)	23,820				
First Cost (a)	$182,620				
First Cost (20-year life; 10% interest) (182,620 x 0.11746)		21,450	0.059	0.016	19.23
Operator (one man-hour per day; $13 per day)		4,745	0.013	0.003	4.24
Normal O&M (2% of 158,800)		3,176	0.009	0.002	2.93
Power ($0.05 per kwhr; brine pump; 10 kwhrs per day)		183	0.001	0.000(3)	0.36
Resin Replacement (three-year life)		16,900	0.046	0.012	14.99
Chemical (salt at $37 per ton) (b)		16,814	0.046	0.012	14.99
TOTAL		$63,268	$0.173	$0.046	$56.38

(a) Does not include legal, administrative, interest during construction, or land. Equipment cost based on vendors' quotations.

(b) For removal of 30-mg/l nitrate.

(c) Plant capacity factor = 100% of 1 mgd or 365 MG per year.

Brine Disposal Costs

Brine disposal costs are not included in the above cost estimate table because of the different disposal facilities available for each community. In McFarland, a plant is being planned and waste will be disposed through the local municipal waste treatment plant to irrigated crops. The quantity of waste will not be detrimental to the crops, and soil and groundwater quality will be monitored. If more plants will be built in the future, waste disposal by evaporation or trucking brine to a local disposal site will be required.

Disposal of waste to a local irrigation water supply system is also a possibility in McFarland that will be explored in the future.

Brine evaporation for the above plant would require a lined pond to evaporate approximately 6,000 gallons of brine per day or 6.7 acre-feet per year. (The major portion of wash water can be handled by the municipal waste disposal system.) In McFarland, this would require an approximately 1-acre lined pond, brine lines, and trucking of evaporated waste to a nearby disposal site. Disposal of evaporated brine should not exceed cost of regenerant chemical since disposal sites are normally closer than sources of salt.

SECTION 8

COST ESTIMATES FOR SYSTEMS USING REVERSE OSMOSIS

R.O. SYSTEM ONLY

For comparison to ion exchange cost of an R.O. system and its operation can be made. Significant differences exist between the two processes and equipment to make use of R.O. more expensive. Based on the experience gained in McFarland, R.O. is not reliable for an "on demand" operation. Storage of approximately one-half day's supply of water is believed to be required both before and after the R.O. system to allow as little interruption in operation as possible. More operator time is also required because of maintenance and the complexity of the instrumentation and controls. The system should be housed for protection of membranes and instruments; consequently, more site preparation work is required. The R.O. system can produce less treated water from a 1-mgd well because of the larger amount of waste brine. Operating cost estimates are given in Table 17.

TABLE 17. OPERATING COST ESTIMATE FOR REVERSE OSMOSIS FACILITIES

			Cost per Unit Quantity of Treated Water (c) ($)		
		Annual Cost	Per 1,000 Gallons	Per Cubic Meter	Per A-F
Equipment and Installation (a)	$705,000				
Engineering 15%	105,750				
First Cost (b)	$810,750				
First Cost (20-year life; 10% interest) (810,750 x 0.11746)		95,231	0.348	0.092	113.41
Operator (eight man-hours per day at $13/hour)		37,960	0.139	0.037	45.30
Normal O&M (at 2% of $705,000)		14,100	0.051	0.013	16.62
Power (at $0.05 per kwhr)		70,000	0.255	0.067	83.10
Chemicals (sulfuric acid at $70 per ton and HMP at $720 per ton)		9,500	0.035	0.009	11.41
Membrane Replacement three-year life		45,000	0.164	0.043	53.45
TOTAL		$271,791	0.992	0.262	323.29

(a) For removal of 30 mg/l nitrate from 750,000 gpd of 1-mgd well. Cost includes R.O. system $450,000, storage tanks $180,000, site preparation $25,000, building $25,000, field piping and wiring $25,000. Based on vendors' quotations.

(b) Does not include legal administrative, interest during construction, and land.

(c) Plant capacity factor assumed to be 100%; therefore, annual water production rate is 750,000 x 365 = 274 MG per year.

Use of R.O. also presents a brine disposal problem to a small community. In McFarland, California, the municipal waste treatment plant has a capacity of 0.5 mgd. The above R.O. system would produce 0.25 MG of waste brine, far too much to discharge to the waste treatment plant. Yearly waste is 280 acre-feet requiring approximately a 47-acre evaporation pond. In McFarland, the brine could possibly be blended with irrigation water supplies for disposal.

R.O. SYSTEM FOLLOWED BY ANION EXCHANGE

From the above cost estimates for operating the two different systems, the cost of a combined system can be estimated. The costs would be those of Table 17 combined with Table 16 with a downward adjustment for the savings realized by reducing ion exchange brine by 90 percent and eliminating any extra operator time for the ion exchange system.

The operating cost for treating 1,000 gallons by the R.O. - ion exchange system would be:

	$/1,000 gallons
Cost for R.O. operation (based on Table 17)	0.992
Cost for I.X. operation (based on Table 16)	0.173
Less 90% of regenerant cost	(0.041)
Less operator cost	(0.013)
Total Operating Cost	$1.111

These costs do not include disposal of approximately 260,000 gallons of waste brine per day.

The advantage of the combined process is that low nitrate and low TDS product water is obtained and could be blended. If blended (one volume raw water to two of treated water), cost would not be less than 74 cents per 1,000 gallons of blended water.

SECTION 9

NITRATE-SELECTIVE RESINS

NITRATE SELECTIVITY - ADVANTAGES AND GENERAL CONCEPTS

Investigators of nitrate ion exchange phenomena are familiar with the interference other ions exert on nitrate removal by anion resins. All major anions found in groundwater consume resin capacity although not to the same degree (see Figure 30). This reduces nitrate removal efficiency of the resin and increases quantity of regenerant chemicals.

It is understandable that various investigators sought some ideal "nitrate-selective resin" as remedy for the observed process inefficiencies and complexities. Such a resin could remove nitrate ions only and allow other anions to pass; thus preserving some original qualities of the untreated water. At the end of the run, the resin would be nitrate loaded making the regeneration of resin more efficient.

However, in practice with available resins, interfering ions cannot only alter quality of product water but also present the possibility of producing a higher nitrate level if the nitrate breakthrough is exceeded. This latter effect is called "reverse adsorption" or "autoregeneration" and can occur if sulfate ion is present. The product water differs from treated water by having bicarbonate, nitrate, and sulfate partially or completely replaced by chloride. In some cases, this can result in a water exceeding secondary chloride standards and a water low in bicarbonate and high in pH and corrosivity. The higher the affinity of the resin for nitrate compared to other ions, the fewer product water quality problems will be encountered.

Nitrate-selective resins also offer regenerant savings. In general, the more nitrate on a resin at the end of the run the more nitrate will be removed per pound of regenerant. Whether or not a given resin is fully loaded with nitrate, 4 to 6 bed volumes of 6 percent salt are required to effect regeneration. It is also apparent that in choosing a resin which gives high nitrate loadings one does not also choose a resin that is more difficult to regenerate, thus obviating the advantage of the more nitrate-selective resin. "Nitrate selective" is terminology which can imply both advantages and disadvantages.

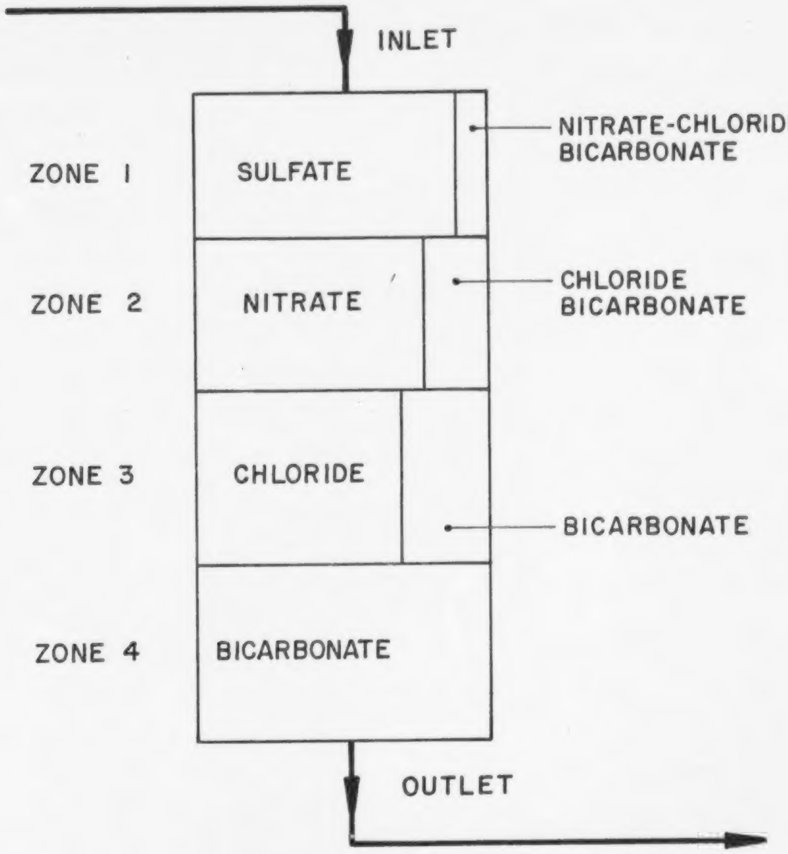

INLET
ZONE 1
SULFATE
NITRATE-CHLORIDE BICARBONATE
ZONE 2
NITRATE
CHLORIDE BICARBONATE
ZONE 3
CHLORIDE
BICARBONATE
ZONE 4
BICARBONATE
OUTLET

FIGURE 30: CHROMATOGRAPHIC ENRICHMENT OF GROUND WATER ANIONS IN AN ANION EXCHANGER

There is also confusion in the literature over this terminology and "electroselectivity." The latter term is a concentration effect which produces a selectivity reversal making any resin more selective for a monovalent ion over a divalent ion as discussed in Reference 1. This effect follows directly from resin-ion equilibria relationships rather than from an inherent resin property. For example, from equilibria between resin, nitrate, and sulfate ions, Equation (1) is derived (Reference 1).

$$\frac{\overline{X_S}}{(1 - \overline{X_S})^2} = K_N^S \frac{\overline{C}}{C} \frac{X_S}{(1 - X_S)^2} \qquad \text{Equation (1)}$$

where Xs and $\overline{Xs}$ are equivalent fractions of sulfate in solution and on resin,

$\overline{C}$ is resin capacity,

C is total aqueous anion concentration, and

K_N^S is an equilibrium constant which expresses selectivity of sulfate over nitrate for a given resin.

The nitrate preference of the resin is not only favored by low K_N^S values but by large values of C as well. If C is large enough, selectivity reversal can actually occur and cause sulfate to break through before nitrate. Work of Buelow et al. (Reference 13) was done to investigate a reportedly nitrate-selective resin. It was shown that the nitrate selectivity was not found at normally occurring feedwater concentrations but only at concentrations over thousands of ppm. Dalton (Reference 20) reports similar findings for feedwaters of 2,000 to 3,000 ppm. These are obvious cases of electro-selectivity being mistaken for nitrate selectivity implying a property of a resin rather than a concentration effect.

The value of increased nitrate selectivity in giving greater resin capacity was challenged by Clifford (Reference 14) who studied nitrate-to-sulfate selectivity of 32 resins and drew a surprising conclusion "Sulfate/nitrate selectivity was nearly irrelevant in determining the average equivalent fraction of nitrate on the resin at the end of a run." This is confirmed by a simple model formulated by Anderson (Reference 21) and discussed in Reference 1. The final expression is given in Equation (2) as

$$BV(N) = \frac{\overline{C}}{a + b + b/n} \times 10^3 \qquad \text{Equation (2)}$$

where BV(N) is bed volumes to nitrate breakthrough;

a, b, and n are concentration related terms.

The fact that no K_N^S occurs in this expression supports Clifford's conclusion. The Anderson model is based on the use of resins at low feedwater concentrations which show preferential sulfate-to-nitrate adsorption. It, therefore, appears valid that increases in nitrate-selective properties of resins will be to no avail unless certain threshold values are exceeded and a selectivity of nitrate over sulfate (or selectivity reversal) occurs without assistance from high ionic concentrations.

DEFINITION OF NITRATE-SELECTIVE RESIN

From the above discussion, it is apparent that some confusion exists in the published literature over terminology used to express nitrate-selective properties of resins. A definition of a nitrate-selective resin is here formulated for the purpose of clarity in the remainder of this report.

Nitrate-selective resin is defined as a resin which in a column operation with common groundwaters retains nitrate as the last ion to break through when exchanging ions at anionic strengths of 10 meq/l. The latter concentration is chosen as a convenient and practical concentration. At very low anion concentrations (especially sulfate), the term "nitrate-selective resin" loses practical significance or fades in importance because relatively large volumes of water can be treated with a given resin bed. At high concentrations, electroselectivity will produce the selectivity reversal; consequently, the column operation should be assessed at anion concentrations more typical of groundwaters. It is pointed out that the definition follows the normally observed breakthrough order when only monovalent ions are present.

A quantitative measure of nitrate-to-sulfate selectivity is the selectivity coefficient together with the anion exchange capacity and anion solution concentration of exchanging ions. Referring to Equation (7) of Appendix 1, Equation (3) can be written

$$\frac{K_S^N C}{\overline{C}} = \frac{\dfrac{X_S}{(1 - X_S)^2}}{\dfrac{\overline{X_S}}{(1 - \overline{X_S})^2}} \qquad \text{Equation (3)}$$

If according to the above definition the resin is nitrate selective, X_S will be larger than $\overline{X_S}$; consequently, for a nitrate-selective resin

$$\frac{K_S^N C}{\overline{C}} = 1 \text{ or greater} \qquad \text{Equation (4)}$$

When C is 10 meq/l

$$\frac{K_S^N}{\overline{C}} = 0.1 \text{ or greater} \qquad \text{Equation (5)}$$

By this measurement, any resin with $K_S^N / \overline{C}$ over a value of 0.1 will be a nitrate-selective resin.

A convenient indicator number of nitrate-to-sulfate selectivity (NSS) for a resin can be formulated from Equation (5)

$$NSS = \log K_S^N - \log \overline{C} + 1 \qquad \text{Equation (6)}$$

where $\overline{C}$ is expressed in meq/l.

If NS = 0 or greater, the resin will be a nitrate-selective resin.

It can be easily seen from Equation (6) that resins with a low C favor a high NSS.

For nitrate-to-chloride selectivity, refer to Equation (2) of Appendix 1. For a nitrate-selective resin

$$K^{N}_{c} = 1 \text{ or greater} \qquad \text{Equation (7)}$$

No resin capacity or ionic strength terms are included. It is also noted that K^{N}_{C} is greater than 1 for known resins. The nitrate-to-chloride selectivity index (NCS) is

$$NCS = \log K^{N}_{C} \qquad \text{Equation (8)}$$

and is zero or greater for a nitrate-selective resin.

PREVIOUS ATTEMPTS AT MAKING NITRATE-SELECTIVE RESINS

Extractant-in-Bead Approach

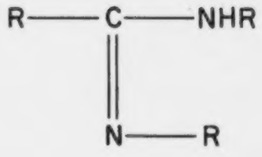
Grinstead and Jones (Reference 15) report the investigation of using porous polymer beads containing a water-immiscible extractant for removal of nitrate from wastewaters. The extractants investigated were the alkyl substituted amidines. Structure 1.

The substituents R and R' were C_8 through C_{12} hydrocarbon radicals including straight chain and cyclic varieties. These compounds are strong bases and can exist as ionized salts in the 7 to 8 pH range. The amidines behave as stronger bases toward nitric acid than other acids. The amidimium salt is more stable as nitrate than as chloride, sulfate, or bicarbonate. Typical K^{N}_{C} values were ranged from 15 through 40 and log K^{N}_{S} values were 5 to 6 (NSS = 1.69 to 2.69).

The objective of this work was to increase K^{N}_{C} of an ion exchanger for removal of nitrate from wastewaters of high chloride content and thereby obtain better efficiency. Loss of extractant from the polymer beads to the product stream and the low ion exchange capacity of the resin of below 0.2 eq/l were the observed disadvantages of the process. The high K^{N}_{C} of the resin precluded the possibility of obtaining high nitrate concentrations in the waste regenerant. The use of ammonium hydroxide as a regenerant produces ammonium nitrate as waste.

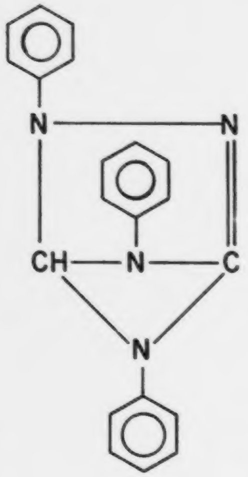
Nitrate Reagents in Ion Exchange Resins - the Salinogen Approach

Basic salinogens are a group of organic compounds which form insoluble compounds with nitrate. The best known is the reagent nitron which is 4,5-dihydro-1,4diphenyl-3,5-phenylimino-1,2,4 triazole which has been used for gravimetric nitrate determination (Reference 22). See Structure 2.

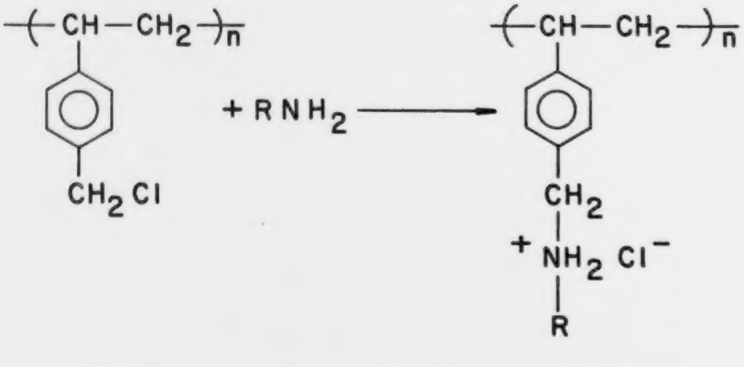


$R-C(=N-R)-NHR$

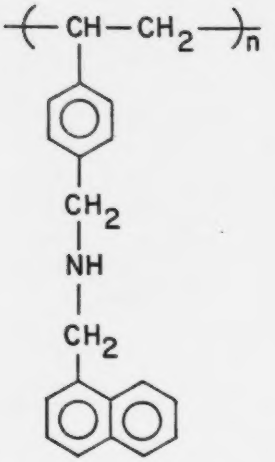
STRUCTURE 1



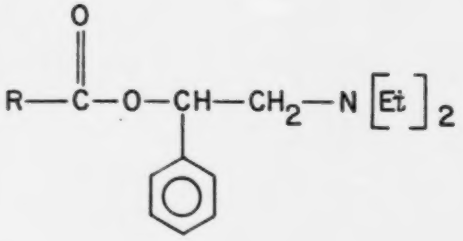
STRUCTURE 2



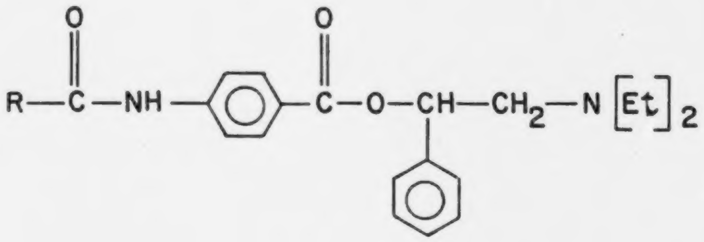
STRUCTURE 3



STRUCTURE 4



STRUCTURE 5



STRUCTURE 6

R= RESIN BACKBONE

The approach of Walitt and Jones (Reference 18) was to incorporate nitrate analytical reagents into the polystyrene structure to make an anion exchange resin selective for nitrate. However, the research led to the use of a group of different amines which were nitrate precipitants. The resins prepared by reacting these amines with the chloromethylated polymer were weak-base anion exchangers with different substituent R groups as shown in Structure 3.

A resin with K^N_C value of 14 resulted when R was 1-naphthylmethyl (1-NMA) giving the Structure 4. Column tests showed that in the free base form, the 1-NMA resin was capable of removing all nitrate from a solution containing 5.6 meq/l of nitrate and 28 meq/l of chloride at pH 2. In comparison, a commercial secondary amine resin (Duolite A7) removed only 65 percent of the nitrate. However, the volumetric capacity of the 1-NMA resin was 36 percent of the Duolite A7.

The hope to use the resin in practice vanished when regeneration of the resin to the free base form was found to be erratic. Regeneration to the chloride form with hydrochloric acid was found to be partially successful but uneconomical.

The report states "It appears that we have chosen to examine in depth a specific example of the proposed concept which was far too successful; that is, the affinity of the 1-naphthylmethylamine group (in the polystyrene resin) for nitrate ion is so great that regeneration to the free base by ordinary methods is unsuccessful."

Although considered unsuccessful, the research is important in showing how nitrate selectivity can be changed by changing the R group of Structure 3. Table 18 shows this variation.

TABLE 18. CAPACITIES AND SELECTIVITY COEFFICIENTS FOR NITRATE OVER CHLORIDE OF RESINS DERIVED FROM CHLOROMETHYLATED POLYSTYRENE AND SELECTED PRIMARY AMINES

Primary Amine	Capacity (meq/g)	Selective Coefficient (K_C^N)
Benzyl	2.25	2.7
4-Chlorobenzyl	1.69	7.6
4-Methoxybenzyl	2.17	3.1
1-Naphthylmethyl	1.85	14.0
Isopropyl	2.59	7.0
n-Butyl	2.67	1.4
t-Butyl	2.51	7.0
n-Hexyl	0.98	6.4
Cyclohexyl	2.21	6.7
n-Octyl	1.07	4.3
Duolite A7	7.00	3.8
Rexyn 203	4.94	4.7

From this data, it is noted that the order of nitrate selectivity increase among simple aliphatic substituents is n-Butyl, n-Hexyl, Isopropyl = t-Butyl. A series with increasing steric requirements near the functional amine group. Unfortunately, no work was done on nitrate-to-sulfate selectivity.

Kansas Water Resources Institute Research

Work of Meloan (Reference 16) also took the approach of incorporating nitrate analytical reagents into a resin structure. A resin with acyl chloride functional groups was reacted with alcohols having various amine groups to form the resin ester bearing amine. In other cases, resin acetamides were used as intermediates to form more complex amides containing amino groups. Bio-gel resins were used in the latter synthesis sequence. The anion exchange resins obtained had tertiary amine exchange sites with two ethyl groups attached. The more complete structures are shown as Structures 5 and 6.

The results gave resins with approximately 50 percent of the resin sites being converted to the amines, and only 10 percent of the amine sites were useful for nitrate exchange. The resins did, however, show a greater exchange capacity for nitrate than phosphate, carbonate, nitrite, or sulfate. The exchange capacity for nitrate was only 0.005 meq per gram of resin making the resin unusable in practical applications.

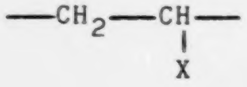
In more recent research (Reference 17), efforts were made to increase the capacity of the resins by using other polymer systems in conjunction with nitron (Structure 2) attempts to introduce a polymerizable vinylic functional group into nitron failed. Condensation polymerization was only marginally successful giving an anion exchanger with very low capacity. Derivatives of nitron were reacted with preformed polymers of p-chloromethylpolystyrene which was obtained by chloromethylation of polystyrene. This approach was only partially successful in that the granulated polymers became tacky when contacted with water. For testing the polyvinylbenzyl chloride resin had to be placed on inert supporting material, such as silica gel. The polymer was found to have a higher preference for absorbing nitrate than other ions including sulfate and was regenerable with the ammonium chloride.

It is difficult to evaluate these resins because no actual column capacities, breakthrough curves, selectivity coefficients, or quantities are reported. No column runs were made with mixtures of ions to determine column retention of nitrate in preference to other ions. All column runs were made with one anion type and the column in the chloride form. The data do show that nitrate was absorbed on nearly 70 percent of the polymer sites. From the data given, it is estimated that the silica-supported polymer system would have an ion exchange capacity of 0.33 meq per liter. This should be compared to 1,000 meq per liter and greater for commercial resins.

The approach of Walitt and Jones (Reference 18) described above had some parallels in that they used nitrate precipitants other than nitron and used preformed beads of divinylbenzene-polystyrene polymer as starting material. They were able to obtain usable polymer beads; however, regeneration was difficult and capacity was low.

Recent Patent

A recent U.S. patent (Reference 23) was issued on the synthesis of ion exchange resins having the substituted amidine group incorporated into the resin. See Structure 1. This approach is based on work of Grinstead and Jones (Reference 15) described above. The patent describes the method of resin preparation by introduction of the amidine groups into a preformed polymer which is preferably a vinyl polymeric matrix cross linked by divinylbenzene, resulting in the recurring structure



$$-CH_2-\underset{\displaystyle X}{\underset{|}{CH}}-$$

where X is the amidine group.

It was found that the best balance between nitrate selectivity and ease of regeneration is obtained when the total number of carbon atoms on the amidine is 5 to 7. Butyl and ethyl groups are generally preferred.

K^N_C values are reported to be 7 to 10. No K^N_S values are reported nor are any column tests or regeneration efficiencies reported. Consequently, it is assumed that although the resins were made the actual use of the resins had not been investigated. Inquiry to the Diamond Shamrock Co. in the United States concerning these resins led this author to believe the resins were not considered commercially feasible products.

NITRATE SELECTIVITY STUDY - THIS PROGRAM

Initial Approach of Research Program

At the beginning of this research program, the approach was to select a strong-base anion exchange resin for pilot tests based largely on commercial availability, long-term usage in water treatment industry, experience of previous investigators, and manufacturers' recommendations. As a result, the resins listed in Table 19 were selected for preliminary screening. No plans were made or thought of diverting any effort to study the possibility of restarting the search for a nitrate-selective resin. It was a general concensus among resin manufacturers representatives and others associated with the program that high nitrate selectivity would not be found in any available strong-base resin and a search for one would merely repeat the frustations of the past. Consequently, the following five resins were screened with laboratory column tests to select one for pilot column testing.

TABLE 19. STRONG-BASE ANION EXCHANGE RESINS

Manufacturer's Designation	Quaternary Amino Type	Porosity Type	Advertised Capacity (meq/ml)
Duolite A-101D	I	Semiporous	1.30
Duolite A-104	II	Micro	1.50
Dowex SAR	II	Micro	1.40
Amberlite IRA-900	I	Macro	1.00
Amberlite IRA-910	II	Macro	1.00

However, as results of these tests became available, a pattern emerged which aroused interest in the synthesis of a nitrate-selective resin. The need for a nitrate-to-sulfate selective resin was particularly desirable because of the high sulfate content of our research well. Column test results coupled with certain results of Clifford's work (Reference 14) led to conclusions concerning molecular structure of the resin and nitrate selectivity. These conclusions departed from approaches of previous workers (described above) who believed that nitrate-selective analytical reagents or extractants need be incorporated into a resin. The procedure and results of the column testing was reported in Reference 1. Some of these results are repeated here but are given a broader interpretation concerning nitrate selectivity.

Indications of Nitrate Selectivity in Column Tests

As pointed out in Reference 1, chromatographic separation of the common anions is expected to occur when treating groundwaters of low ionic concentrations (say 10 meq/l) in a column of strong-base anion exchange resin. This chromatographic enrichment is depicted in Figure 30 as would be expected for a resin having the normal order of increasing selectivities: bicarbonate, chloride, nitrate, sulfate. At nitrate breakthrough, the column will have Zone 1 and Zone 2 only with some small amounts of chloride and bicarbonate in each and some nitrate in Zone 1. For a given feedwater, as the nitrate-to-sulfate selectivity increases, the nitrate in Zone 2 diminishes and nitrate in Zone 1 increases (resin capacity remaining constant). Evidence for the partitioning of ions is obtained from breakthrough curves of column tests. From these test results it appeared that some factors were contributing to increased nitrate-to-sulfate selectivity among strong-base resins. Several tests were made using 2-inch-diameter columns with a 24-inch bed depth of resin. The test procedures are described in Reference 1 and were conducted with Well 3 water and synthetic blends to determine column capacity with these waters and verify estimates of column capacity. Test results and conditions are shown in Table 20 and Figures 31 through 40.

Inspection of the breakthrough curves shows the formation of nitrate enriched zones only under certain conditions. Run 02199 (Figure 31) and Run 02219 (Figure 32) were both run with the same feedwater composition; however, Figure 32 shows nitrate breakthrough occurring well before sulfate breakthrough along with a nitrate peak above the influent concentration. This breakthrough pattern is to be expected when a sulfate enriched zone is formed at the top of the column and a nitrate enriched zone is formed at the bottom. As the sulfate enriched zone grows after nitrate breakthrough, sulfate ion displaces the resin-bound nitrate in the nitrate zone. The nitrate effluent concentration will exceed the influent concentration because of this displacement by sulfate. A different effluent profile is obtained with the Type II resin, A-104, in Run 02199 (Figure 31) which shows a nearly simultaneous breakthrough for nitrate and sulfate ions indicating that the enriched sulfate and nitrate zones do not occur at these concentrations. This indicates the selectivity under these conditions for the Type I resin is $SO_4^= > NO_3^-$ and for the Type II resin is $SO_4^= = NO_3^-$. In Run 03059

TABLE 20. ION EXCHANGE COLUMN EXPERIMENTS WELL 3 AND SYNTHETIC MIXTURES

Run No.	Resin I.D.	Resin Type	Exh. Rate (BV/m)	Feedwater Composition (meq/l) NO	HCO	Cl	SO	Bed Volumes to Break-through SO	NO	Figure No.
11078	A-101D	I	.33	1.56	1.63	2.51	5.93	ND[a]	157	None
02199	A-104	II	.33	1.11	2.39	2.01	4.68	242	240	8-2
02219	A-101D	I	.33	1.17	2.39	2.01	4.68	232	198	8-3
03059	A-104	II	.33	1.91	2.39	2.82	6.70	165	172	8-4
03299	Dowex SAR	II	.33	1.73	2.73	2.67	7.65	183	184	8-5
06229	IRA-900	I	.33	1.79	2.49	2.82	7.18	138	140	8-6
06279	IRA-910	II	.33	1.79	2.49	2.82	7.18	133	122	8-7
02290	A-101D	I	.36	1.17	1.74	2.67	7.32	163	147	8-8
02260	A-101D	I	1.10	1.26	1.61	2.72	7.74	174	159	8-8
02230	A-101D	I	1.56	1.48	1.39	2.56	6.87	188	176	8-8
03069[b]	A-101D	I	.33	0.85	1.50	1.45	3.35	ND	300	8-11
03050[b]	A-101D	I	.33	1.63	1.14	1.41	3.64	318	248	8-9
03140[b]	A-101D	I	1.0	1.12	1.08	2.33	8.33	168	163	8-10

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[a] Not determined.

[b] Synthetic blends.

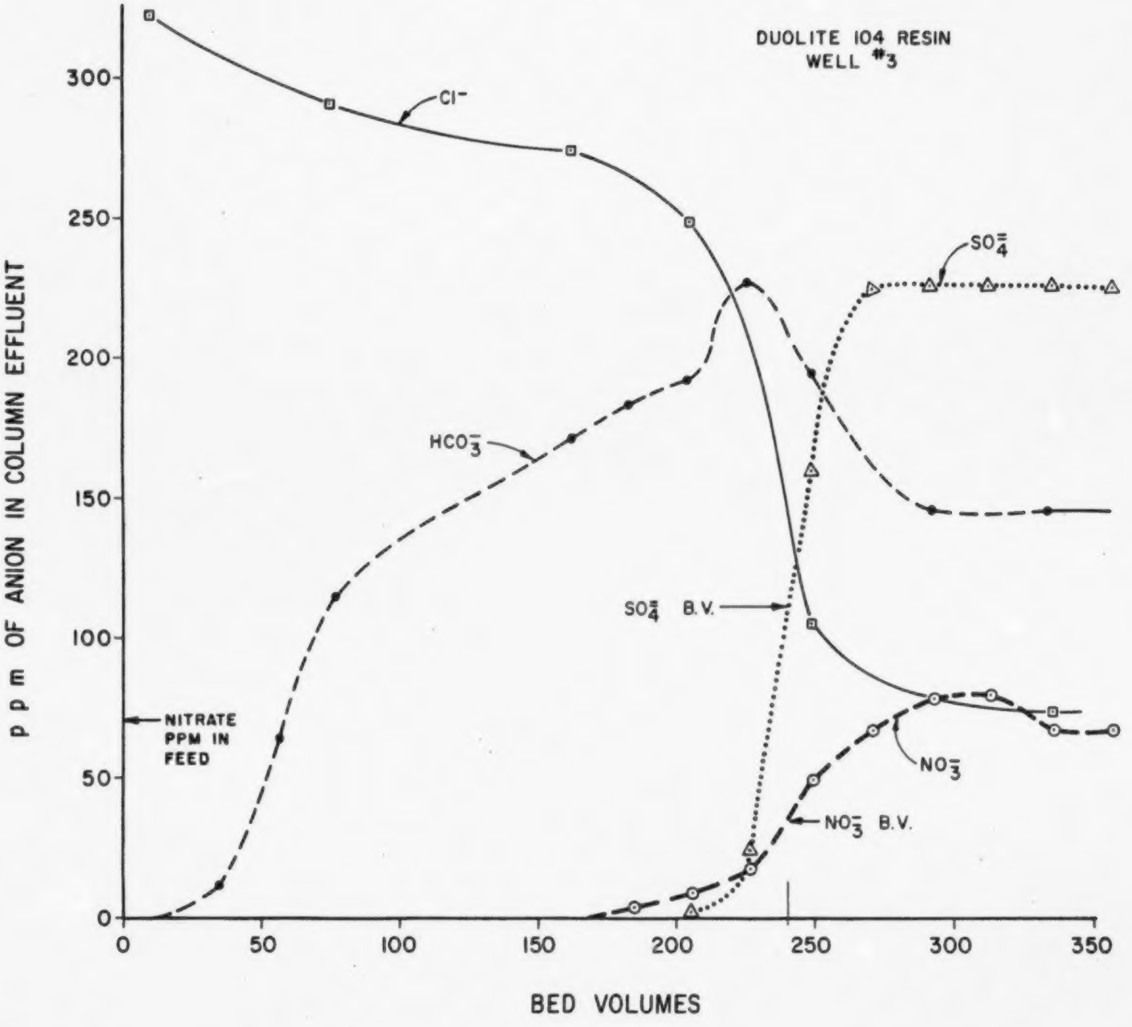


FIGURE 31 ION EXCHANGE COLUMN EXPERIMENT 02199

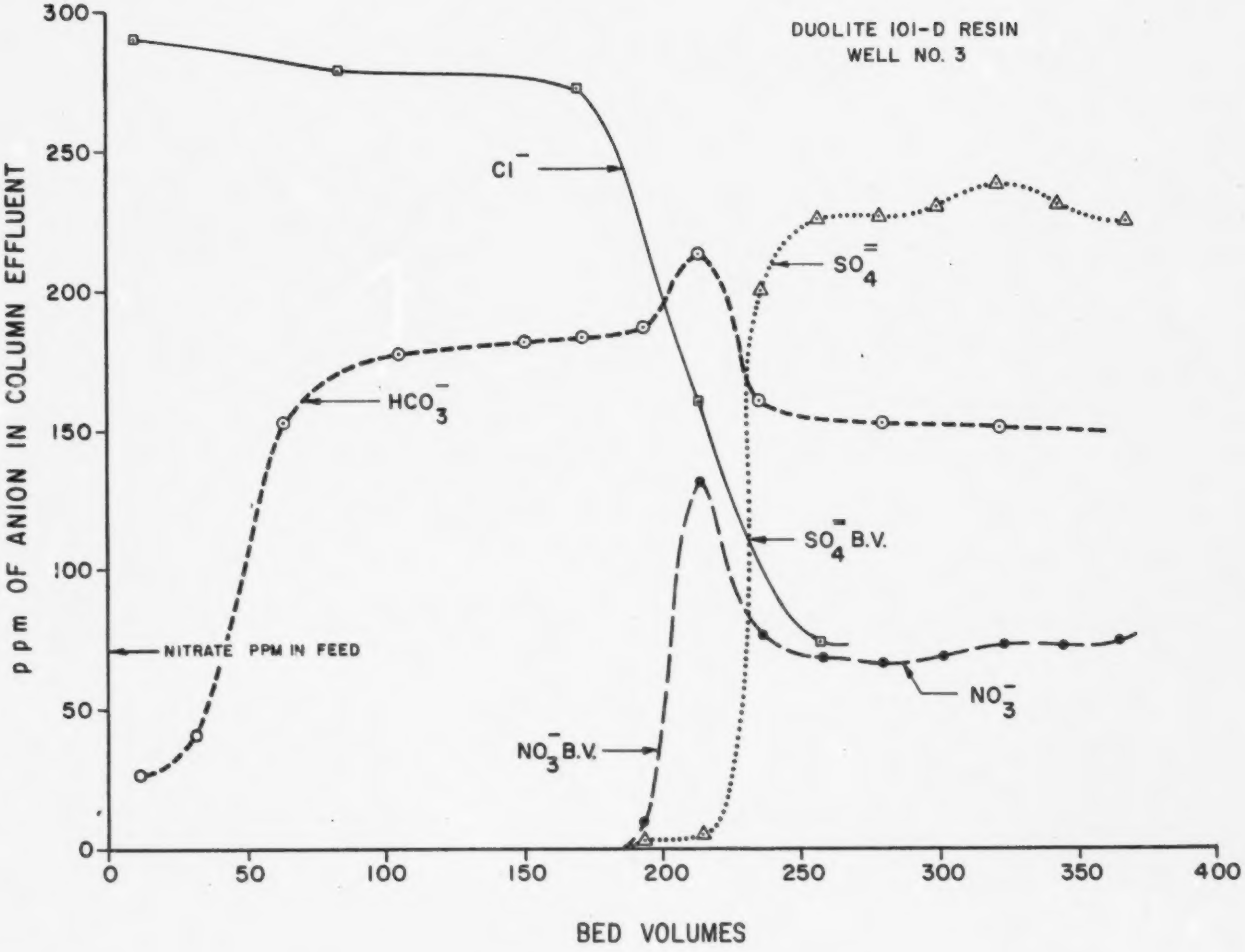


FIGURE 32 ION EXCHANGE COLUMN EXPERIMENT 02219

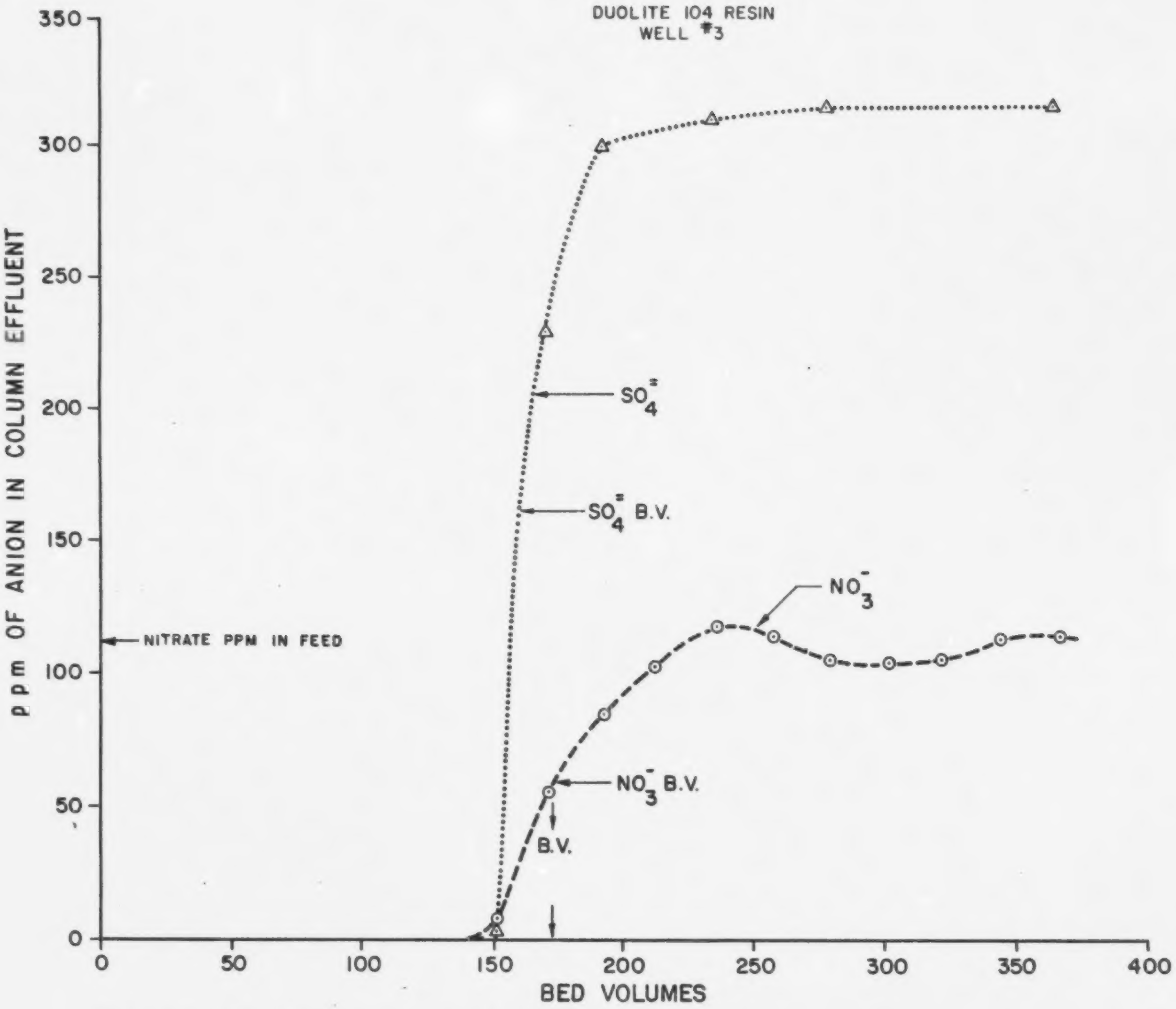


FIGURE 33 ION EXCHANGE COLUMN EXPERIMENT 03059

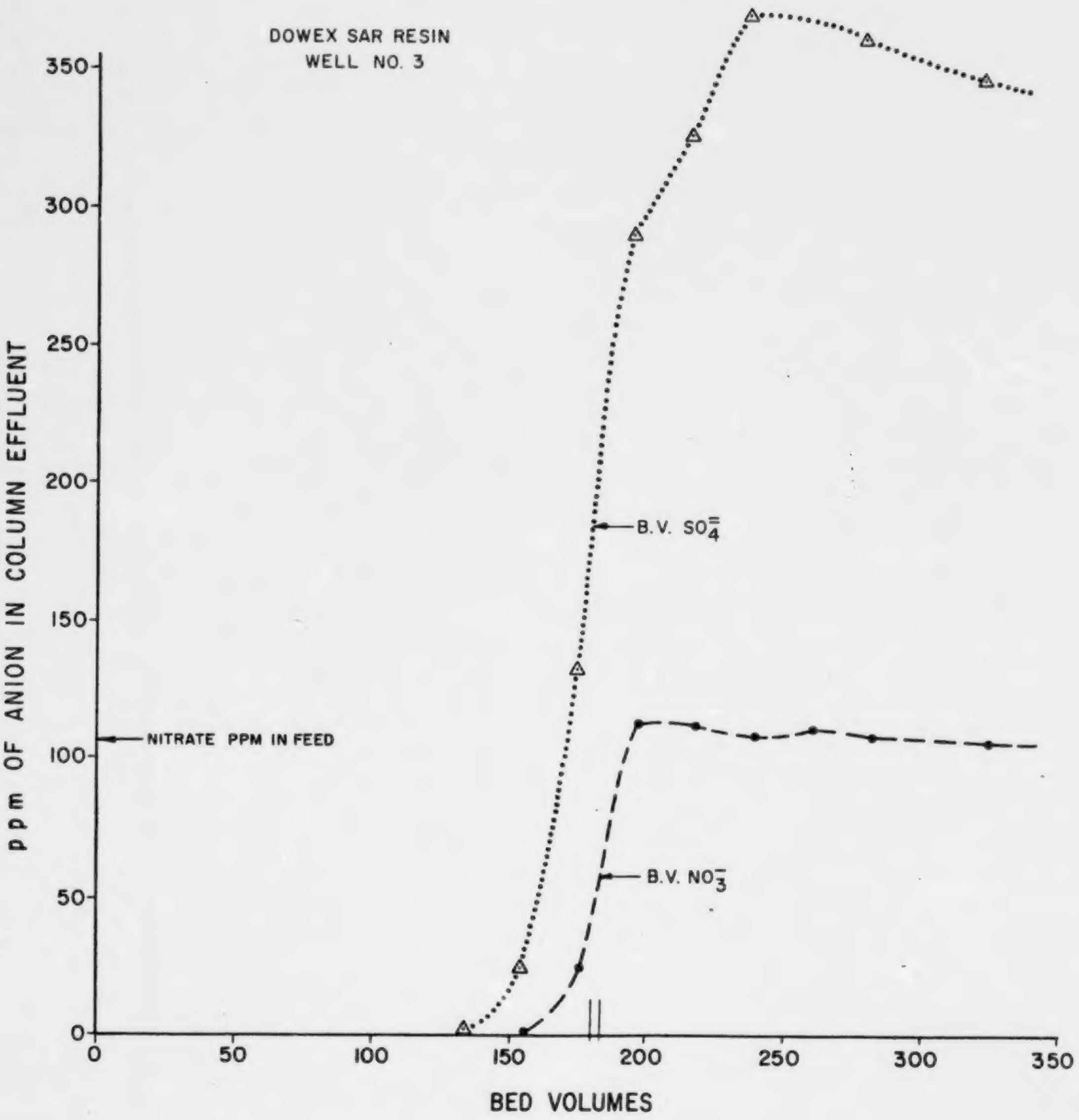


FIGURE 34 ION EXCHANGE COLUMN EXPERIMENT 03299

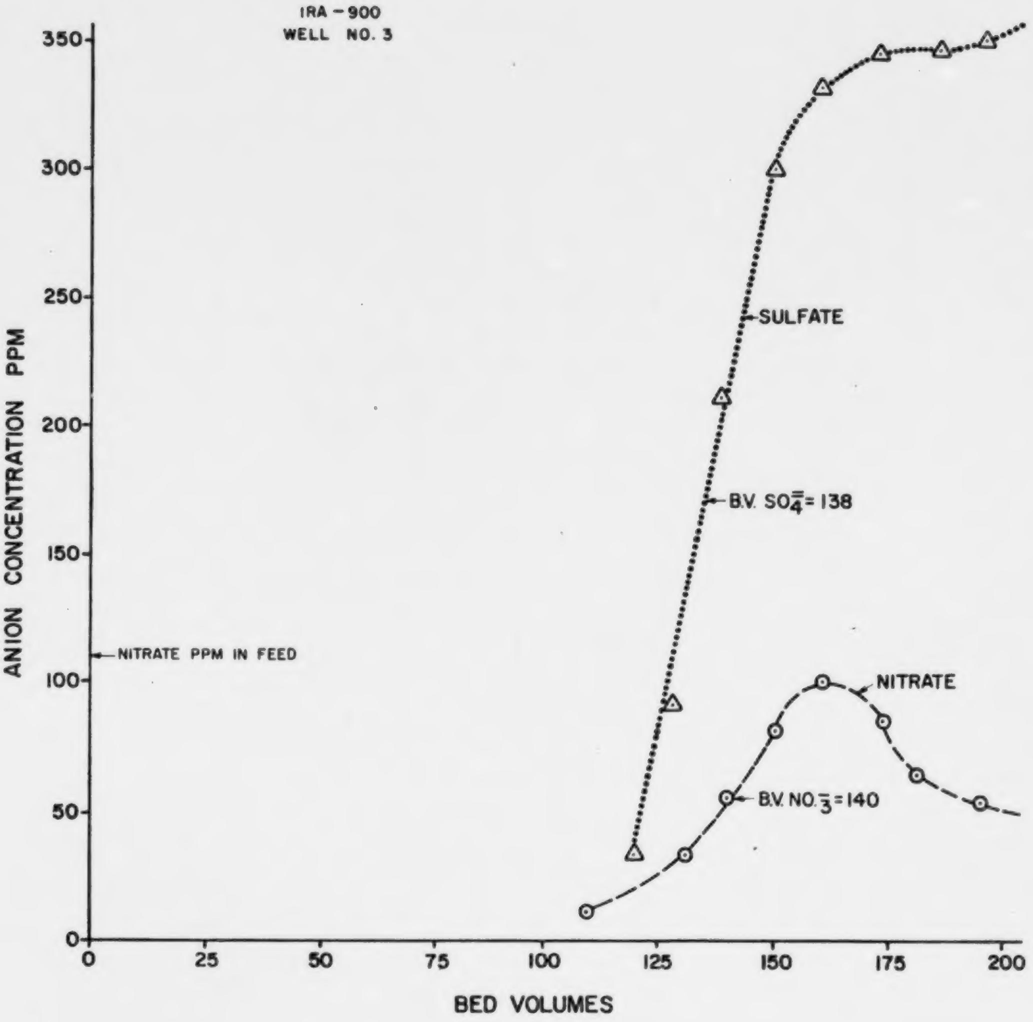


FIGURE 35 ION EXCHANGE COLUMN EXPERIMENT 06229

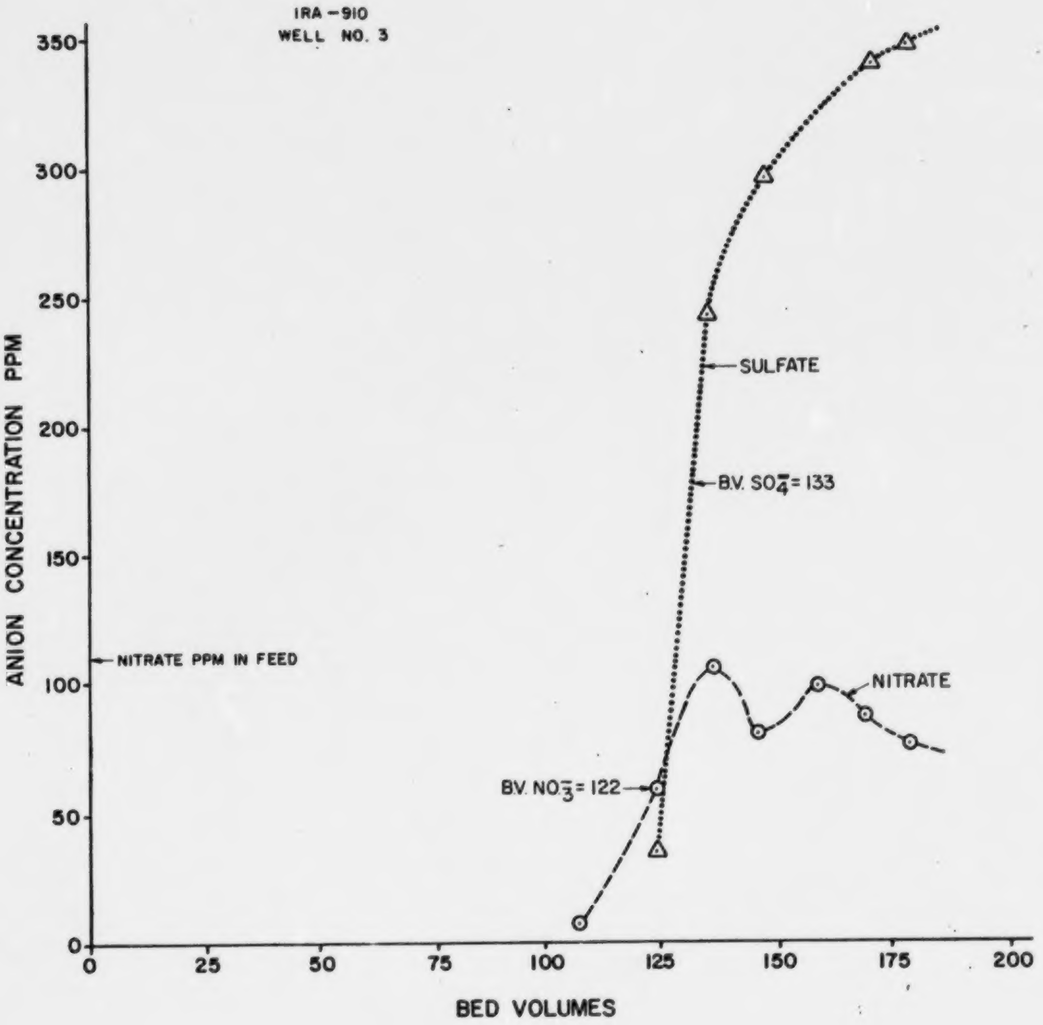


FIGURE 36 ION EXCHANGE COLUMN EXPERIMENT 06279

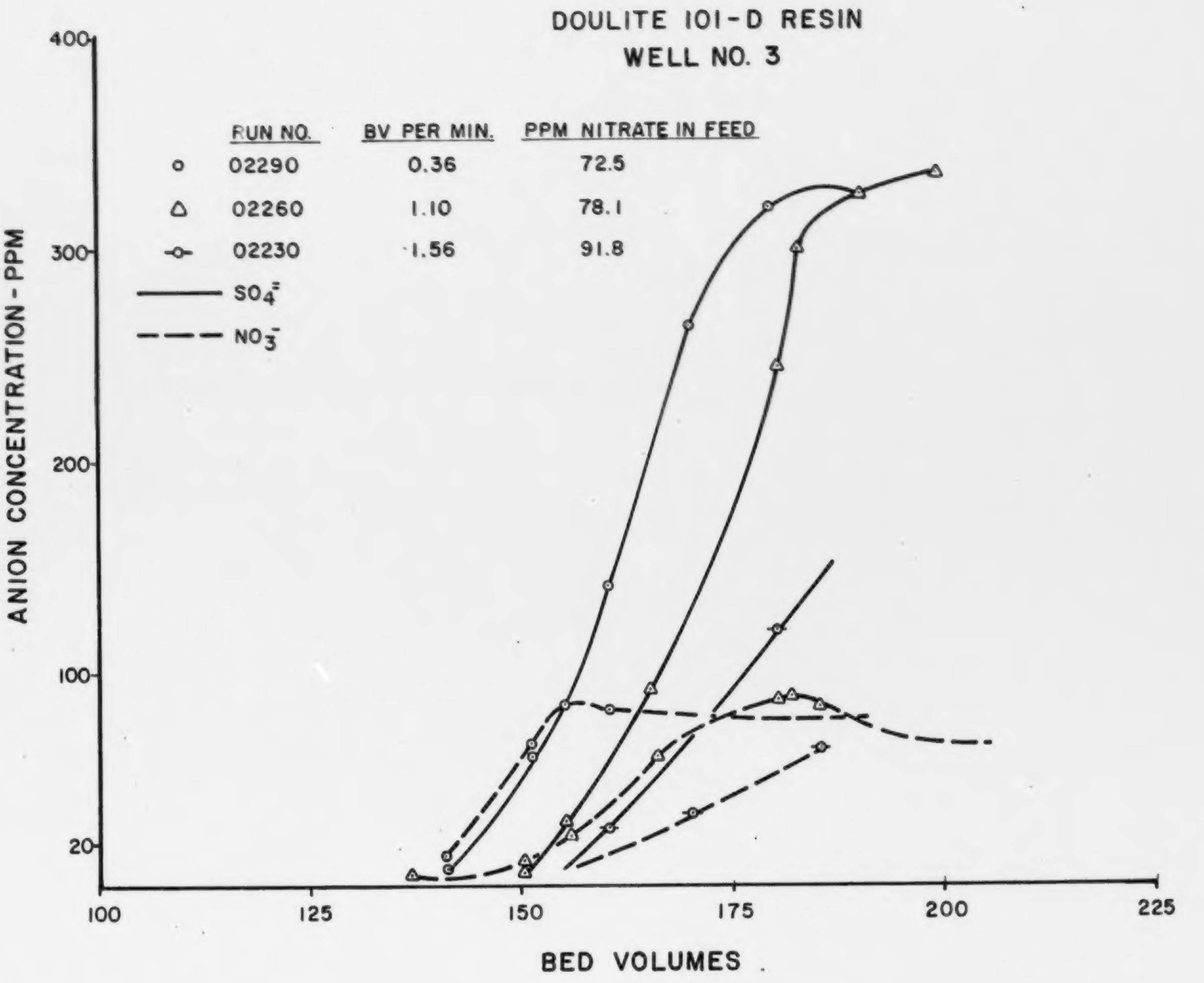


FIGURE 37 ION EXCHANGE COLUMN EXPERIMENTS - FLOW RATE EFFECT

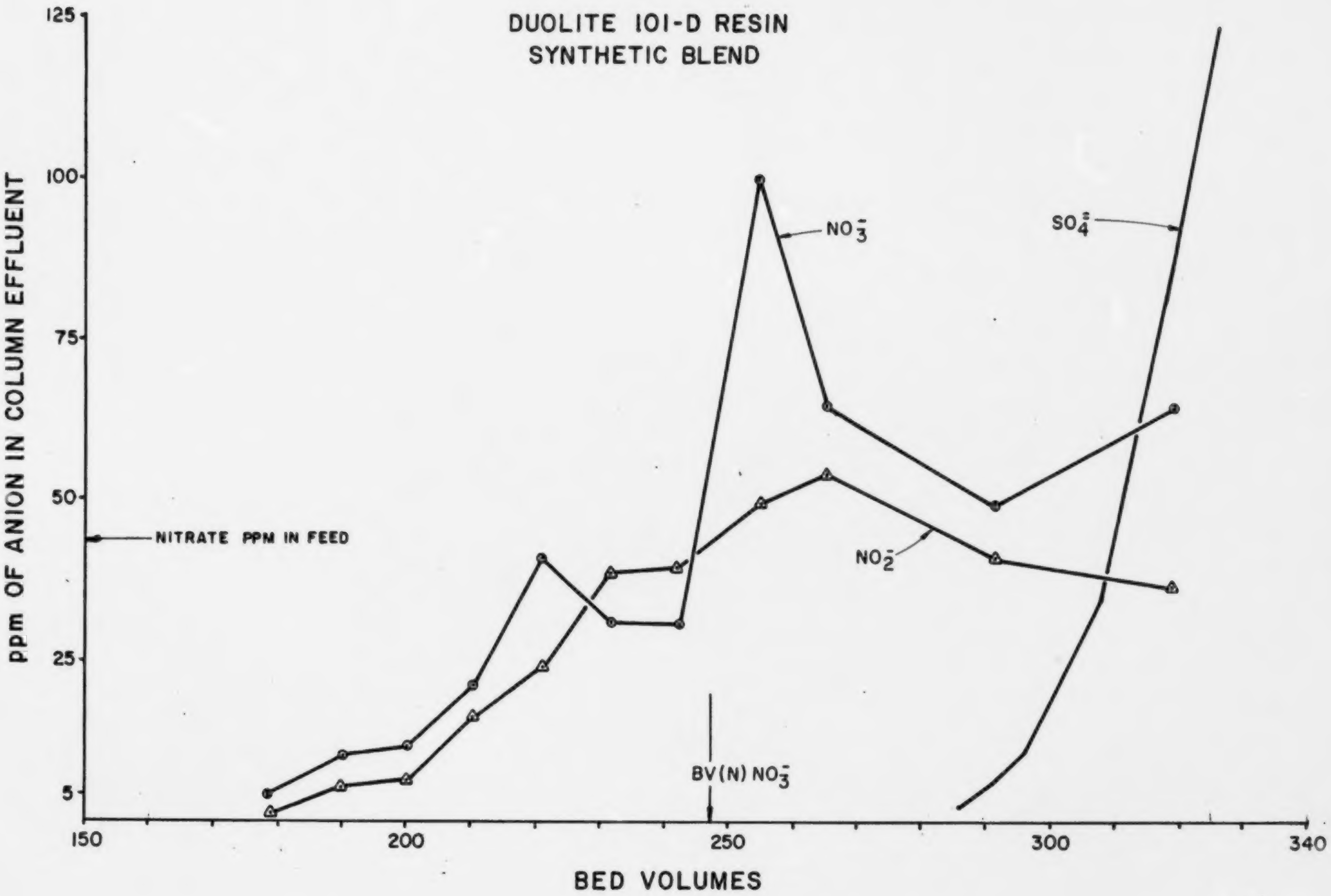


FIGURE 38 ION EXCHANGE COLUMN EXPERIMENT 03050

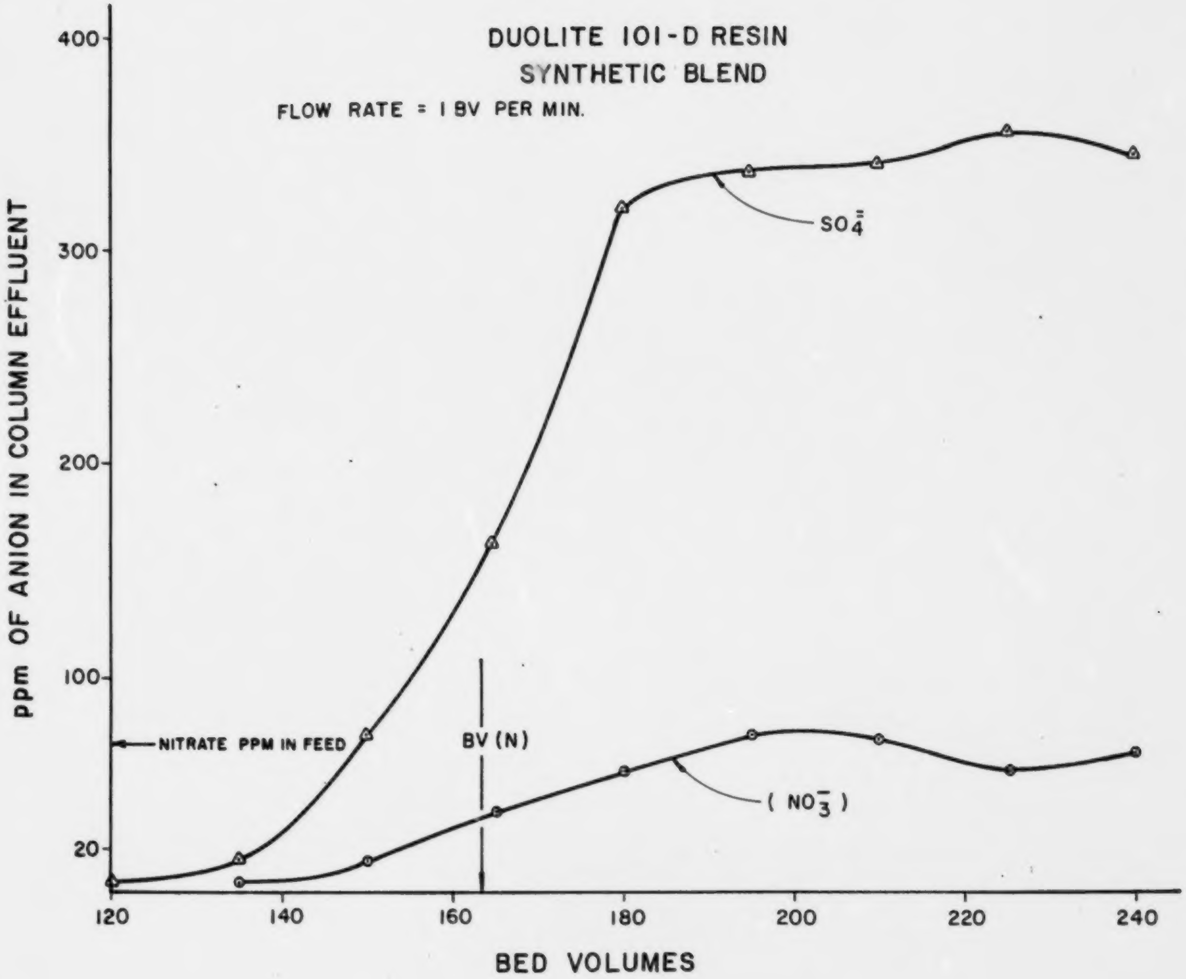


FIGURE 39 ION EXCHANGE COLUMN EXPERIMENT 03140

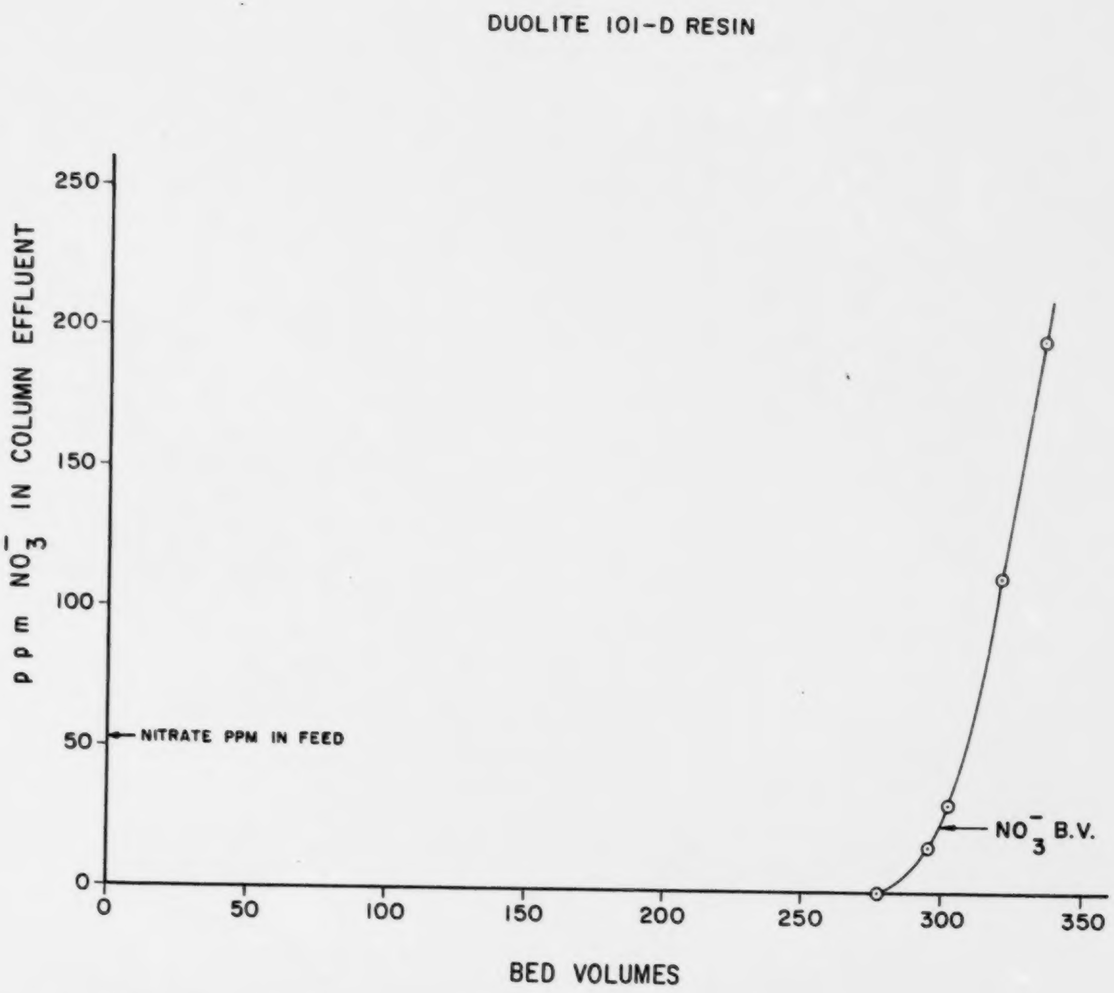

DUOLITE 101-D RESIN

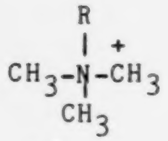
FIGURE 40 ION EXCHANGE COLUMN EXPERIMENT 03069

(Figure 33) with the Type II resin, sulfate ion breakthrough occurs before nitrate. Run 03299 (Figure 34) shows the same behavior as A-104 resin. Resins A-101D, A-104, and Dowex SAR are of the microporous type. When the macroporous resins are compared, nitrate and sulfate breakthrough occurred nearly simultaneously without nitrate effluent concentration exceeding the influent concentration for both Type I and Type II resins (Runs 06229 and 06279, Figures 35 and 36); thus indicating that chromatographic partitioning does not occur with the macroporous resins at these concentrations.

Run 02290 (Figure 37) with A-101D resin showed nitrate breakthrough prior to sulfate, but the rise of effluent nitrate concentrations above influent concentration is not as apparent as in Run 02219. Run 03050 (Figure 38) shows the typical breakthrough pattern of the A-101D resin; however, Run 03140 (Figure 39) does not which can be attributed to nonequilibrium at high flow rates. No sulfate breakthrough was determined in Run 03069 (Figure 40), but partitioning is evident from the high nitrate peak.

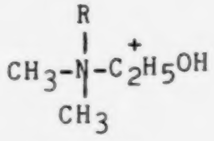
The conditions under which chromatographic partitioning did or did not appear as indicated by column effluent profiles are compared in Table 21. Only one resin, A-101D, has thus far exhibited an effluent pattern suggestive of chromatographic separation. At flow rates above 0.33 BV per minute (Runs 02260, 02230, and 03140), the chromatographic pattern either does not occur or is distorted by high flow rates.

These results indicate differences between A-101D and the other resins may be significant in considering nitrate-to-sulfate selectivity. The differences between the resins are moisture content, degree of cross linking, capacity, and the type of pendant groups on the quaternary nitrogen as shown below:



$CH_3-\underset{CH_3}{\overset{R}{N^{+}}}-CH_3$

Type I
A-101D and IRA-900



$CH_3-\underset{CH_3}{\overset{R}{N^{+}}}-C_2H_5OH$

Type II
A-104, SAR, and IRA-910

Duolite A-101D differs from the Type II resins in chemical structure. It was suspected at this point that the greater steric requirements of the ethoxy group could be a factor. The difference in results between A-101D and IRA-900, both Type I, is apparently due to the type of porosity as determined by degree of cross linking. This difference determines how the resin imbibes or holds water within it. Microporous resins are more homogeneous, single-phase structures with low cross linking

TABLE 21. COMPARISON OF COLUMN EXPERIMENTS

Run No.	Effluent Pattern Suggestive of Chromatographic Partitioning	Resin (Type)	Resin Porosity*	meq SO_4	meq NO_3	meq SO_4 / meq NO	Flow Rate BV/min
11078	---	A-101D(I)	micro	5.93	1.56	3.81	.33
02199	No	A-104(II)	micro	4.69	1.11	4.23	.33
02219	Yes	A-101D(I)	micro	4.69	1.11	4.23	.33
03059	No	A-104(II)	micro	6.70	1.92	3.49	.33
03299	No	SAR	micro	7.65	1.74	4.40	.33
06229	No	IRA-900(I)	macro	7.18	1.80	3.99	.33
06279	No	IRA-910(II)	macro	7.18	1.80	3.99	.33
02290	Yes	A-101D(I)	micro	7.33	1.71	4.29	.36
02260	No	A-101D(I)	micro	7.75	1.26	6.15	1.10
02230	No	A-101D(I)	micro	6.87	1.49	4.61	1.56
03050	Yes	A-101D(I)	micro	3.64	1.63	2.23	.33
03140	No	A-101D(I)	micro	8.33	1.12	7.43	1.00
03069	Yes	A-101D(I)	micro	3.35	0.85	3.94	.33

---

*Duolite 101D has a moisture content of 48 to 55 percent; Duolite A-104 has moisture content of 40 to 46 percent; Dowex SAR moisture content equals 38 to 45 percent; IRA-900 has a moisture content of 60 to 64 percent; and IRA-910 has a moisture content of 50 to 55 percent.

whereas macroporous resins retain water in pores of the resin which is highly cross linked (15 to 20 percent divinylbenzene) and have two-phase heterogeneity. Both types can have the same water content but higher degrees of cross linking reduce resin swelling (Reference 24).

Low cross linking, microporosity, and low steric requirements around the ion exchange site appeared to be the factors which gave A-101D its higher sulfate-to-nitrate selectivity. The divalent sulfate ion being highly hydrated and sterically hindered would find greater difficulty in entering an anion exchange site which itself is sterically hindered or restricted from swelling by high degrees of cross linking. The A-101D provides both lower steric hindrance and lower cross linking than the other resins, thus giving it higher sulfate-to-nitrate selectivity.

Previous research supports this line of reasoning. Hale et al. (Reference 25) showed that the sorption of quaternary amine cations by cation resins was reduced by both higher cross linking and higher molecular weight of the amine. It was also shown by Wheaton and Bauman (Reference 26) that Dowex 2, a Type II resin, shows a 5.3 percent shrinkage from chloride to nitrate form and a 3 percent swelling from chloride to sulfate form. They note the generalization that greater swelling denotes (relatively) reduced selectivity as work is required to swell the elastic particles.

Indications of Nitrate Selectivity by Departures From Anderson Model

The above qualitative interpretation can be put on a quantitative basis. A simple mathematical model to predict the number of bed volumes to obtain nitrate breakthrough was developed by Anderson (Reference 21) and was discussed in Reference 1. Equation (2) is one form of this model which was based on the chromatographic separation of ions as shown in Figure 30. The model is useful as long as this chromatographic enrichment of nitrate occurs in Zone 2. Equation (2) does not show any dependence of BV(N) on the nitrate-to-sulfate selectivity coefficient. This is due to assumption concerning certain terms which appear in a rigorous formulation. It should also be pointed out that the model has not been widely tested with column data except for data given here and in Reference (1).

A comparison of experimental BV(N) and calculated values from the Anderson model are given in Table 22. The average deviation is -10.87 percent indicating higher nitrate capacity is actually obtained than is predicted by the model.

TABLE 22. ESTIMATION OF COLUMN CAPACITY USING ANDERSON MODEL

Run. No.	Effluent** Pattern Suggestive of Chromatographic Partitioning	BV(N) Exp.	BV(N) Est. Eq. (13)	Percent Deviation $\frac{\text{Est.-Exp.}}{\text{Estimate}} \times 100$
11078	---	157	166	+5.42
02199	No	240	229	-4.80
02219	Yes	198	210	+5.71
03059	No	172	154	-11.69
03299	No	184	143	-28.67
06229	No	140	106	-32.07
06279	No	122	106	-15.09
02290	Yes	147	149	+1.34
02260*	No	159	140	-13.57
02230*	No	176	150	-17.33
03050	Yes	300	289	-3.81
03069	Yes	248	234	-5.98
03140*	No	163	135	-20.74
Average				-10.87

---

*Runs made at high flow velocity.

**See Figure 30.

Runs showing chromatographic partitioning show +0.7 percent deviation from the model. This agreement is to be expected and helps to confirm the validity of the model. Runs which do not show the partitioning show an average deviation of -18.7 percent from the model indicating these resins give higher nitrate capacity than the model predicts. Runs made at high flow velocities with A-101D resin may well deviate because of high flow velocities or nonequilibrium conditions since runs with the same resin gave excellent agreement at low velocity. Other runs made with A-104, IRA-900, and IRA-910 at normal flow velocities indicate that the nitrate-to-sulfate selectivity has exceeded a threshold value to invalidate the Anderson model. Thus nitrate selectivity is beginning to become apparent in those resins whose structures and compositions may influence nitrate selectivity as discussed above.

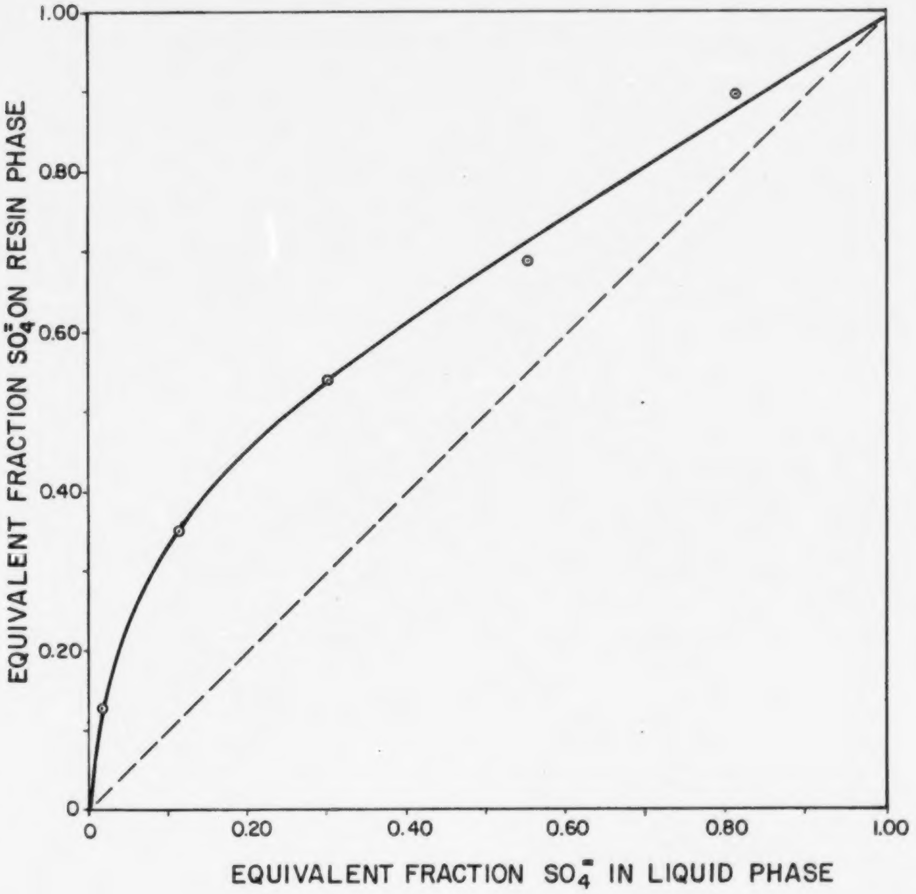
Indications of Nitrate Selectivity in Clifford Isotherms

In a study on nitrate selectivity of 32 commercially available anion resins, Clifford (Reference 14) developed isotherm data from equilibrated mixtures of resin, nitrate, and sulfate ions. Isotherms are given in Figures 41 through 45 for the five commercial resins used on this program. From these data separation factors and selectivity coefficients can be determined. The isotherms are also visual representations of the generally greater selectivity of these resins for sulfate over nitrate throughout the full range of resin loadings of the two ions. The dashed lines of these isotherms represent data which would be obtained provided the resin shows no selectivity for either ion. Furthermore, to have a selectivity coefficient of constant value, the upward bow of the isotherm would be symmetrically displaced from the straight line. Close examination of the curves reveals the unsymmetrical shape of the isotherms indicating a strong selectivity for sulfate ion when the resin is high in nitrate loading with this tendency dropping off as the resin becomes more sulfate loaded. Figure 41 for A-101D shows such a tendency. For A-104, the Type II resin, the tendency is more pronounced giving the curve a slight "S" shape. The tendency reaches an obvious "S" shape for IRA-900, IRA-910, both macroporous resins, and Dowex SAR microporous Type II. These data support the above conclusions concerning structural and cross linking effects on nitrate-to-sulfate selectivity. As these resins become sulfate loaded, swelling occurs causing internal strains in proportion to the sulfate. Strain will also be greater as steric requirements of the amine increase and as resin cross linking increases. Thus, at high sulfate loadings, the macroporous resins and the Dowex SAR become nitrate selective. From visual inspection of these isotherms, an increasing order of nitrate selectivity can be written as shown in Table 23. This ranking is compared to the deviations from the Anderson equation discussed above. The order of nitrate selectivities derived from the isotherms or Anderson equation deviations is identical since negative deviations are interpreted as nitrate selectivity indicators.

TABLE 23. RANKING OF NITRATE-SULFATE SELECTIVITY

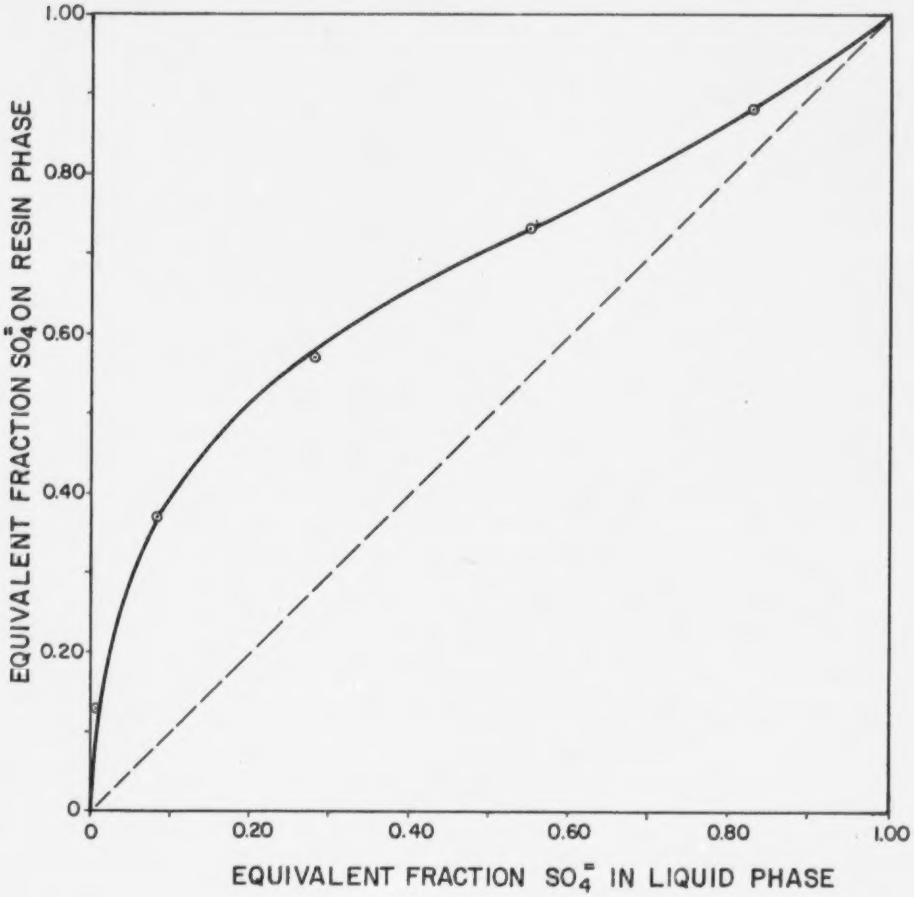
Resin	Relative Nitrate Selectivity From Isotherms	Deviation From Anderson Equation
Duolite A-101D	Least	0.7
Duolite A-104	↓	-8.2
Amberlite IRA-910		-15.09
Dowex SAR		-28.67
Amberlite IRA-900	Most	-32.07

It is also very interesting to notice the shape of the chloride-nitrate isotherms which remain symmetrical or undistorted in those resins showing nitrate selectivity. The inference here is that nitrate-sulfate selectivity can be



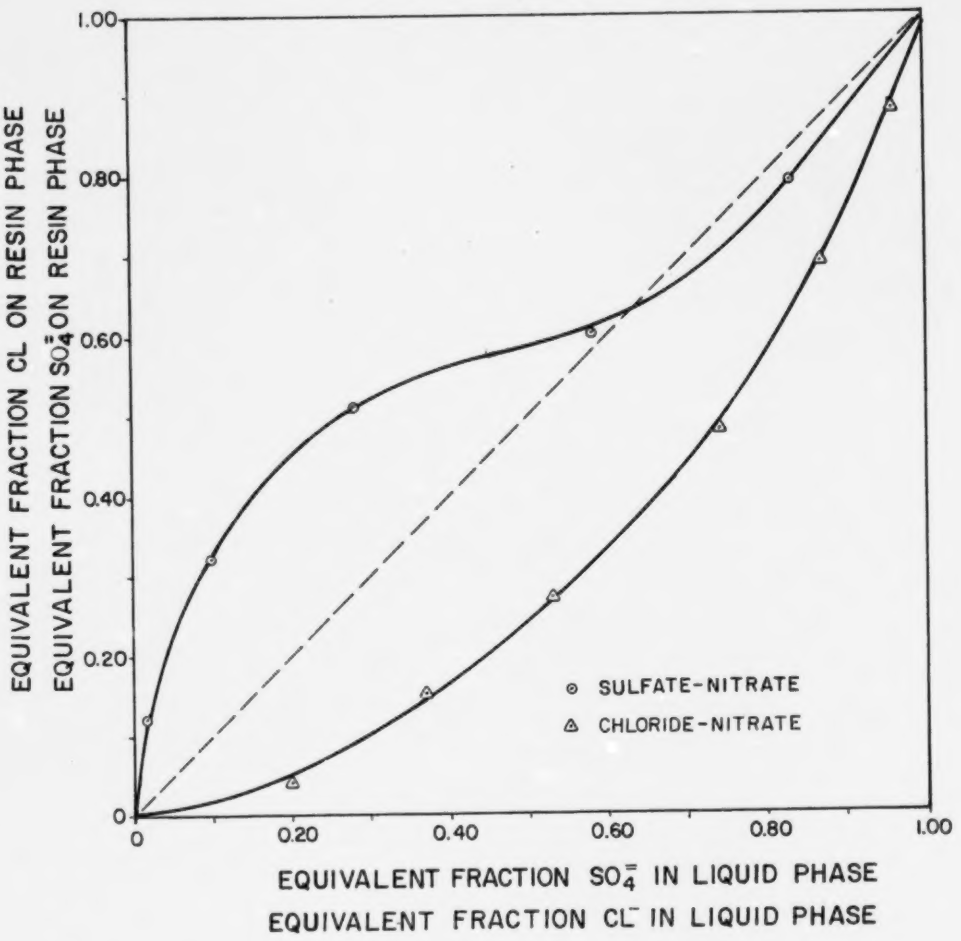
DUOLITE A 101 D, "IMPROVED" POROSITY GEL
STYRENE-DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY

FIGURE 41 25°C BINARY ION-EXCHANGE ISOTHERM



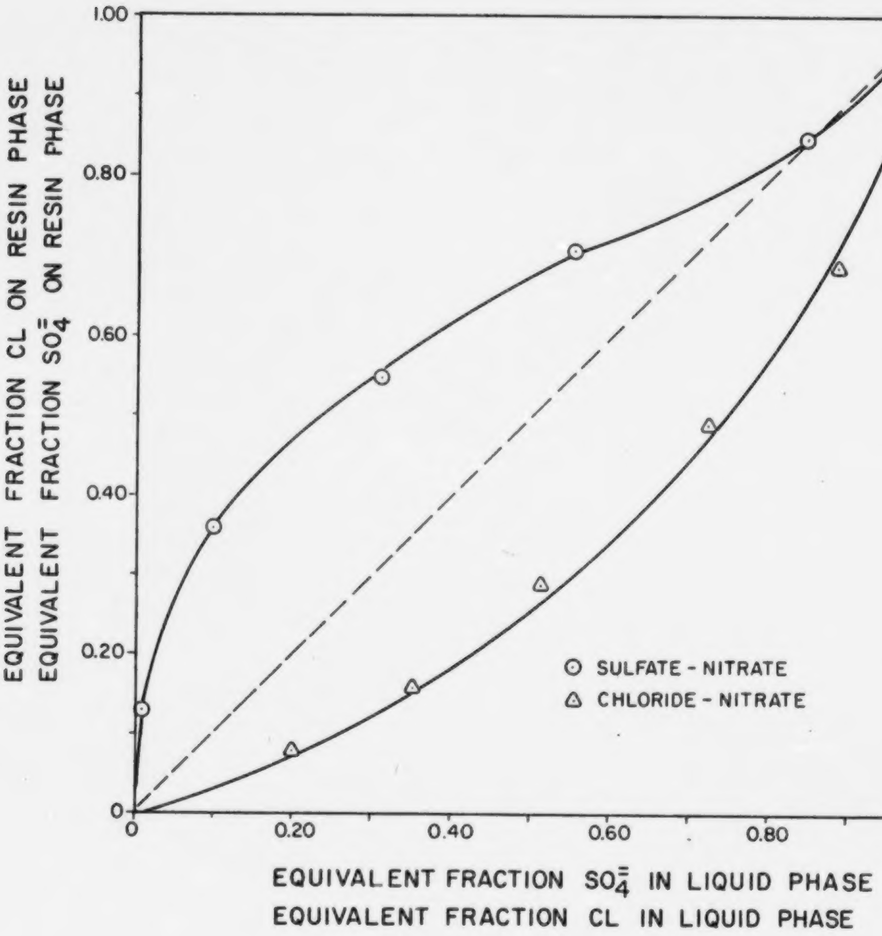
DUOLITE A-104, MICROPOROUS GEL
STYRENE-DVB MATRIX
TYPE I & II QUATERNARY-AMINE FUNCTIONALITY

FIGURE 42: 25°C BINARY ION-EXCHANGE ISOTHERM



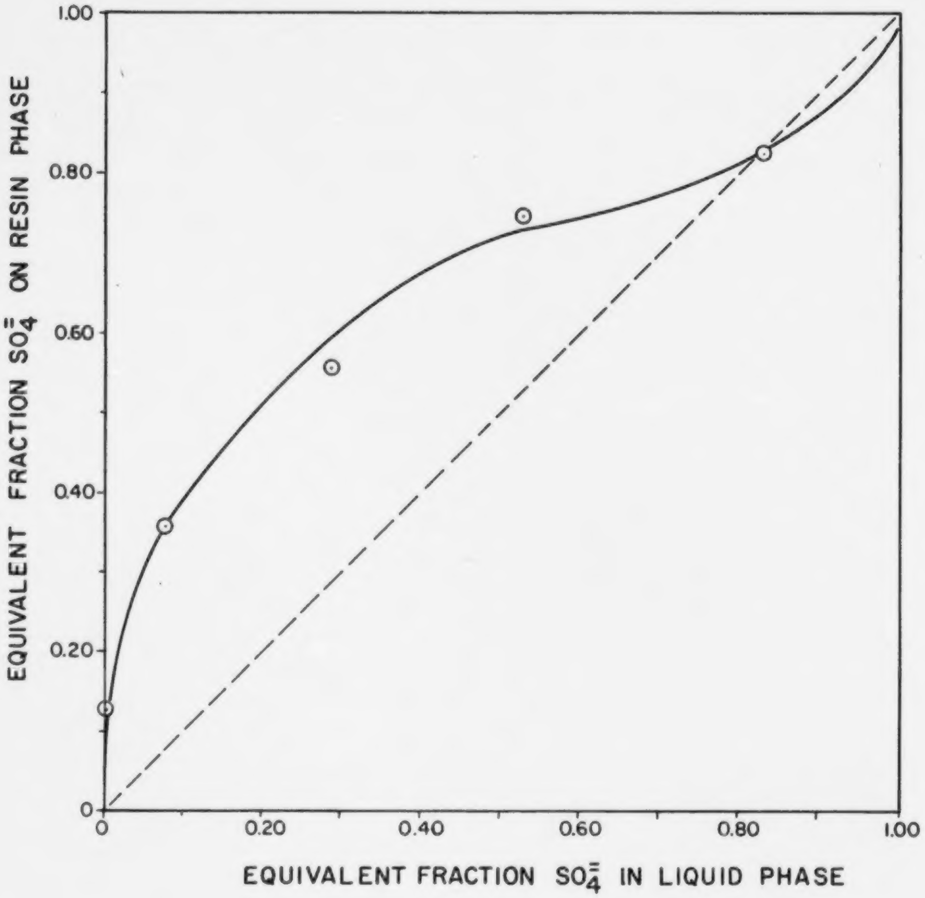
AMBERLITE IRA 900, MACROPOROUS RESIN
STYRENE - DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY

FIGURE 43 25°C BINARY ION-EXCHANGE ISOTHERM



AMBERLITE IRA 910 MACROPOROUS RESIN
STYRENE - DVB MATRIX
TYPE II QUATERNARY - AMINE FUNCTIONALITY

FIGURE 44 25°C BINARY ION-EXCHANGE ISOTHERM



DOWEX SAR, MICROPOUS GEL
STYRENE - DVB MATRIX
TYPE II, QUATERNARY-AMINE FUNCTIONALITY

FIGURE 45. 25°C BINARY ION-EXCHANGE ISOTHERM changed through steric hindrance and cross linking with no effect on nitrate-chloride selectivity, hence such resins should be quite capable of chloride ion regeneration. However, the sulfate-loaded resin should also show a tendency toward higher chloride-sulfate selectivity.

Other strong-base resins showing pronounced "S" shaped isotherms from Clifford's work are Amberlite IRA-410 (microporous, Type II), Ionac A-550 (microporous, Type II). The tendency is also found in some tertiary amine weak-base resins.

Clifford's own analysis of variables influencing nitrate-to-sulfate selectivity was made using isotherm data for 13 weak-base and 19 strong-base resins and is summarized here in Table 24. His analysis does not show any effect of increasing R group size as is indicated in our above analysis. However, the effect was noted in weak-base resins and anion resins in general. His analysis indicates Type I resins to be more nitrate selective than Type II; a conclusion differing from ours. Also his conclusion about type appears inconsistent with his conclusion concerning R group size. He also concludes that increased cross linking favors nitrate selectivity which is in agreement with our observations.

TABLE 24. VARIABLES INFLUENCING NITRATE/SULFATE SELECTIVITY*

++ = Greatly Increases
+ = Increases
0 = No Significant Effect on
- = Decreases
-- = Greatly Decreases
N/A = Not Applicable

	Anion Resins in General (1)	Strong-Base Resins (2)	Weak-Base Resins (3)	Polystyrene Resins (4)	Nonpolystyrene Weak-Base Resins (5)	Type I Strong-Base Resins (6)
Nitrogen in Polymer Backbone	--	N/A	--	N/A	N/A	N/A
Increasing R Group Size	++	N/A	++	++	++	N/A
Increasing Degree of Cross Linking	0	+	0	0	0	+
Macroporous as Opposed to Microporous	0	0	0	0	0	0
Isoporous as Opposed to Gel or MR	N/A	-	N/A	N/A	N/A	--
Increasing Capacity	-	0	-	N/A	N/A	N/A
Type I as Opposed to Type II	N/A	+	N/A	N/A	N/A	N/A
Increasing pKa	+	0	0	0	++	N/A

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*Taken from Reference (14).

Column Test With Nitrate-Selective Sulfate-Loaded Resin

A column experiment was devised to test the above observed nitrate-selective tendency of resins when loaded with sulfate. Dowex SAR resin was put in the sulfate form to determine if nitrate-selective column behavior could be observed.

The 2-inch column was loaded with a 24-inch depth of wet SAR resin in chloride form and treated with sodium sulfate (1,200-ppm sulfate) until effluent and influent sulfate were equal. After washing, the water from Well 3 was pumped through the column at 0.33 BV per minute. The breakthrough curves are shown in Figure 46. The chloride and nitrate curves show the "S" shape of a "self-sharpening" front but with an elongated characteristic indicating importance of kinetic factors or more probably change in selectivity coefficients as sulfate is lost from the resin. For a self-sharpening front to occur when nitrate from solution displaces sulfate from resin

$K_N^S \frac{\overline{C}}{C}$ must be less than one. In the above case, a minimum

value of K_N^S can be estimated

$K_N^S \times \frac{1,400}{10}$ is less than one

K_N^S is less than $\frac{1}{140}$

K_S^N is greater than 140

This differs from published values for K_S^N of 25 for strong-base resins. The value of 143 can be considered the K_S^N value for the resin column when it is high in sulfate, whereas 25 is a value obtained from equilibrium measurements.

A K_S^N value can also be estimated from the breakthrough curves for this resin. Data from Table 19, Run 03299, shows nearly simultaneous breakthrough for sulfate and nitrate. Indicating that $X_S = X_S$ and $X_N = X_N$. Therefore, from Equation (3)

$$K_S^N \frac{C}{C} = 1 \qquad \text{Equation (9)}$$

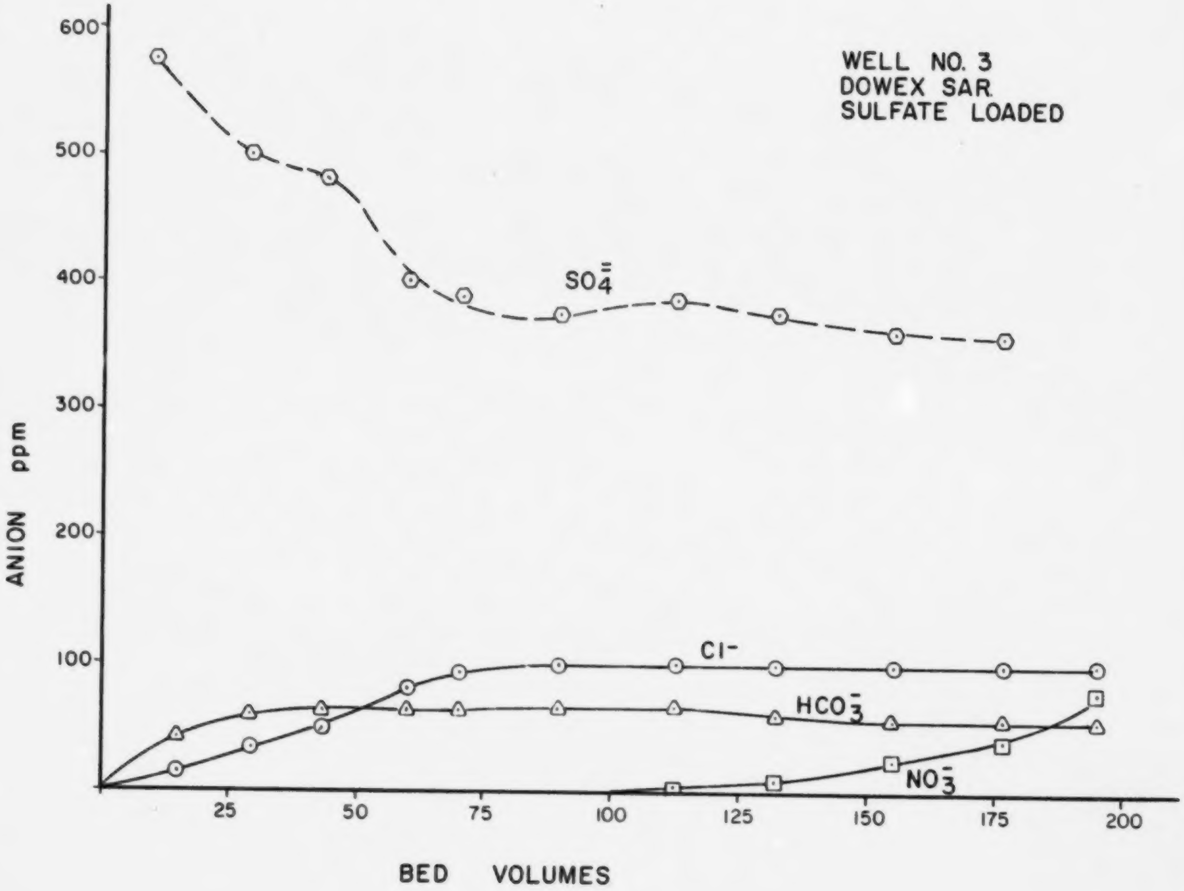


FIGURE 46 NITRATE REMOVAL BY SULFATE LOADED COLUMN

$$K_S^N = \frac{C}{C} = \frac{1,400}{9.38} = 149 \qquad \text{Equation (10)}$$

Which is in good agreement with the above.

Regeneration of the nitrate spent resin which was originally in the sulfate form by sulfate was tested by using dilute solutions of sodium sulfate. The electroselectivity effect can be used here to help shift the resin to the divalent sulfate form by use of dilute regenerants. If a dilute sulfate solution is passed through the above spent column, it can be seen from Equation (3) that the X_S of the effluent is proportional to C. By substituting values into this equation, it is seen that low C values could give very efficient regeneration. X_S is approximately 0.85. If C is 10 meq/l

$$\frac{149 \times 10}{1,400} \times 28.7 = \frac{X_S}{(1 - X_S)^2} \qquad \text{Equation (11)}$$

$$X_S = 0.85$$

The nitrate concentration leaving the column will be 1.5 meq/l or 93 ppm giving 15 percent conversion of sulfate-to-nitrate. If C is 5 meq/l, $X_S = 0.77$, the nitrate concentration leaving the column will be 0.23 x 5 = 1.15 meq/l (71 ppm) or 23 percent utilization of regenerant. The column was treated with these above concentrations. Nitrate effluent concentrations obtained were 80 ppm and 70 ppm compared to 93 and 71 predicted. Lower regenerant concentrations could be used to achieve near stoicheometric displacement of nitrate with sulfate but would require very large volumes of water. As impractical as this appears, the develoment of a sulfate cycle resin and process is attractive in the McFarland situation because of the availability of irrigation water supplies of very low salt content (5 to 15 ppm). The use of sulfate-loaded resins with lower K_S^N values would give nitrate breakthroughs with nonself-sharpening fronts, i.e., a gradual increase in nitrate leakage would occur and lower column nitrate loadings would result.

A general relationship can be written for any resin to aid in estimating the amount of sulfate regenerant required. From Equation (3), it is easily shown that

$$\frac{\dfrac{X'_S}{(1 - X'_S)^2}}{\dfrac{X_S}{(1 - X_S)^2}} = \frac{C'}{C} \qquad \text{Equation (12)}$$

where X_S is equivalent fraction of sulfate in influent water and X'_S is sulfate equivalent fraction in regenerant. C and C' are total anion meq/l in influent and regenerant, respectively. Table 25 gives sample parameters. At high X_N values, it is noted that X'_N is also high indicating very efficient utilization of regenerant.

TABLE 25. PARAMETERS FOR NITRATE REMOVAL USING SULFATE REGENERATION CYCLES

X'_N	X_N	X'_S	X_S	C'/C	BV(R)/BV(N)*
0.8	0.8	0.2	0.2	1	1
0.6	0.6	0.4	0.4	1	1
0.4	0.4	0.6	0.6	1	1
0.2	0.2	0.8	0.8	1	1
0.88	0.8	0.12	0.2	0.5	1.8
0.72	0.6	0.28	0.4	0.5	1.7
0.51	0.4	0.49	0.6	0.5	1.6
0.26	0.2	0.74	0.8	0.5	1.5
0.92	0.8	0.08	0.2	0.1	8.7
0.91	0.6	0.09	0.4	0.1	6.6
0.78	0.4	0.22	0.6	0.1	5.1
0.50	0.2	0.5	0.8	0.1	4.0
0.7	0.8	0.30	0.2	2	0.57
0.52	0.6	0.52	0.4	2	0.58
0.30	0.4	0.70	0.6	2	0.67
0.15	0.2	0.85	0.8	2	0.67
0.54	0.8	0.46	0.2	5	0.30
0.34	0.6	0.66	0.4	5	0.35
0.21	0.4	0.79	0.6	5	0.38
0.15	0.2	0.85	0.8	5	0.27

$$^{*}\frac{BV(R)}{BV(N)} = \frac{C}{C'} \quad \frac{X_N}{X'_N}$$

Resin capacity and selectivity must be considered if self-sharpening fronts are desired. C' (or C) must be low enough to make

$$\frac{K^{N}_{S} \quad C'}{\overline{C}} = 1 \text{ or less for regeneration}$$

$$\frac{K_S^N C}{\overline{C}} = 1 \text{ or more for nitrate absorption}$$

However, as seen in Table 25, it is impractical to use very low C'/C because of high BV(R) requirements. Resins of low K_S^N and high $\overline{C}$ must then be used. If K_S^N is around 140 and $\overline{C}$ is 1,400, the C' threshold value is 10 meq/l. If C is greater than 10 meq/l, a self-sharpening front for nitrate absorption will be obtained, and if C' is less than 10 meq/l, a self-sharpening front will be obtained for regeneration.

In summary, a sulfate cycle is efficient if the spent column is high in nitrate and K_S^N is low. These requirements are incompatible for waters with high sulfates because the spent column will be low in nitrate. For waters with little or no sulfate, a sulfate cycle has greater promise if a nonself-sharpening front can be tolerated in the nitrate absorption cycle. $\overline{X_N}$ must also be fairly high, say 0.5. Treatment with dilute sulfate would first remove chloride and bicarbonate to make $\overline{X_S} = 1 - \overline{X_N} = 0.5$.

For sulfate regeneration, assume that C' = 23 meq/l (saturated calcium sulfate); $\overline{C}$ = 1,300 meq/l; K_S^N = 25 and using Equation (3), X_S in spent regenerant is estimated as 0.25 making X_N = 0.75 or 1,070-ppm nitrate and 276-ppm sulfate both as calcium salts. This would require 38 bed volumes of regenerant having a concentration of 2,000-ppm calcium sulfate. Regeneration efficiency would be 75 percent. However, a supply of low TDS water must be available for regenerant. If the nitrate-laden water has 1.5 meq/l, the amount of water which can be treated would be about 433 BV. Consequently, the volume of regenerant would be less than 10 percent of water treated.

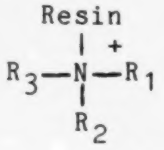
A second possible application of a sulfate cycle would be in combination with a chloride cycle where nitrate and sulfate enriched zone are formed. In this case a resin of low K_S^N is used in the chloride form. At nitrate breakthrough, a nitrate enriched zone occurs at the bottom of the column and a sulfate at the top. Regeneration with a saturated calcium sulfate solution will remove the nitrate as calcium nitrate which is suitable for irrigation. 1.3 BV of 6 percent sodium chloride would be required for sulfate removal and restoring the column to the chloride form. Partial regeneration cycles may reduce regenerant requirements.

Sulfate cycles should be further investigated.

NITRATE SELECTIVITY STUDY OF SPECIAL RESINS

Choice of Special Resins

From the above interpretation of the column data obtained on the five strong-base anion resins and the experiments with the sulfate-loaded column, the possibility of increasing nitrate-to-sulfate selectivity by changing the quaternary amino R group became apparent. A series of resins were proposed for synthesis to study the effect of steric requirements of the R groups about the quaternary ammonium nitrogen in the structure



$$\begin{array}{c} \text{Resin} \\ | \; + \\ R_3\text{—}N\text{—}R_1 \\ | \\ R_2 \end{array}$$

where R groups could be methyl, ethyl, isopropyl, and t-butyl. It was also proposed to test resins with two and three ethoxy groups to determine effect of hydrophilicity. It was by far from certain in which direction nitrate selectivity would change since the difference between methyl and ethoxy (Type I and Type II) was not only one of steric properties but also one of hydrophilicity. It was also uncertain as to the extent nitrate selectivity would change. As indicated above, to make a resin usefully nitrate selective, a threshold K_S^N value must be exceeded to increase the column capacity for nitrate. Thus, the previous attempts to prepare nitrate-selective resins by incorporating nitrate precipitants into the resin were reasonable. The study of the proposed resins was undertaken to merely determine trends in selectivity as structure was varied.

The resins finally selected for study were confined to availability of commercially available tertiary amine intermediates. These amines were reacted with the chloromethylated styrene-divinylbenzene copolymer intermediate used in the commercial manufacture of Duolite A-104 (Type II) resin. Consequently, the trimethyl amine was more highly cross linked than commercial A-101D. The resins were prepared under contract to the Diamond Shamrock Co. of Redwood City, California.

Nitrate-to-Sulfate Selectivity

Samples of resins were put in the nitrate form by passing one normal sodium nitrate solution through a column of each resin. The resins were supplied to us in the chloride form. A measured 5-ml sample of wet resin was placed in a bottle with 150 ml of a sodium sulfate solution of about 50 meq/l. The tightly stoppered bottle was periodically shaken and allowed to stand overnight before sulfate analyses were performed. From the exchange reaction 1/2 $SO_4^{=}$ + RNO_3 = 1/2 R_2SO_4 + NO_3^{-} and where

meqS = meq of sulfate, aqueous phase

meqN = meq of nitrate, aqueous phase

meqS = meq of sulfate, resin phase

meqN = meq of nitrate, resin phase

meqR = meq of resin

$\overline{C}$ = Resin capacity, meq/l

C = Total anion meq/l in aqueous phase

v = Volume of aqueous phase, l

v' = Volume of resin phase, l

the following can be written

$$\overline{meqS} + meqS = Cv$$

$$\overline{X_S} = \frac{\overline{meqS}}{meqR} = \frac{Cv - meqS/l\ v}{\overline{C}v'}$$

$$X_S = \frac{meqS/l\ v}{C}$$

Values of $\overline{X_S}$ and X_S are substituted into Equation (3) for calculating K_S^N. Values of $\overline{C}$ for the resins were obtained from Diamond Shamrock Co.

The resins studied are listed in Table 26 with their molecular structure and designation. The approximate K_S^N values obtained are listed in Table 27 together with other data supplied by the vendor. Data for Duolite A-101D is also given for comparison. Resin No. 6 was also prepared as a control and is the same as Duolite A-104. The vendor also supplied equilibrium data from which binary isotherms can be constructed. These are shown in Figures 47 and 48. An isotherm for R-TEOH was calculated from a K_S^N value of 10 in Figure 48.

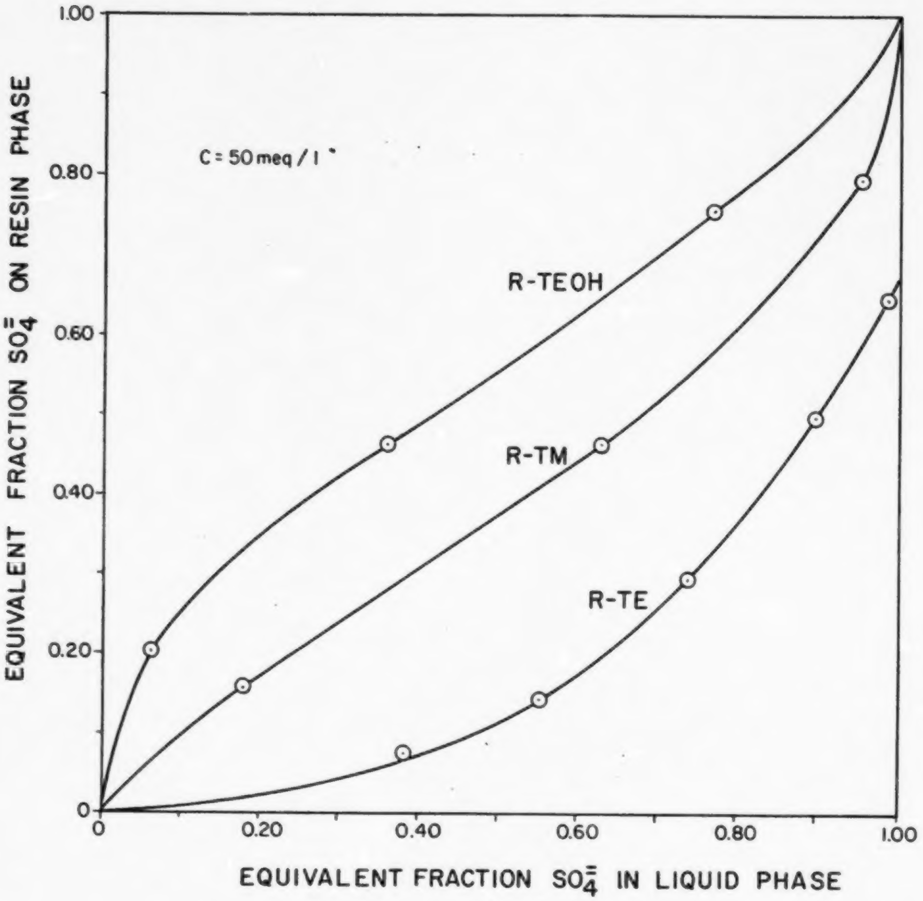


FIGURE 47. SULFATE-NITRATE ION EXCHANGE ISOTHERMS FOR THREE SPECIAL RESINS

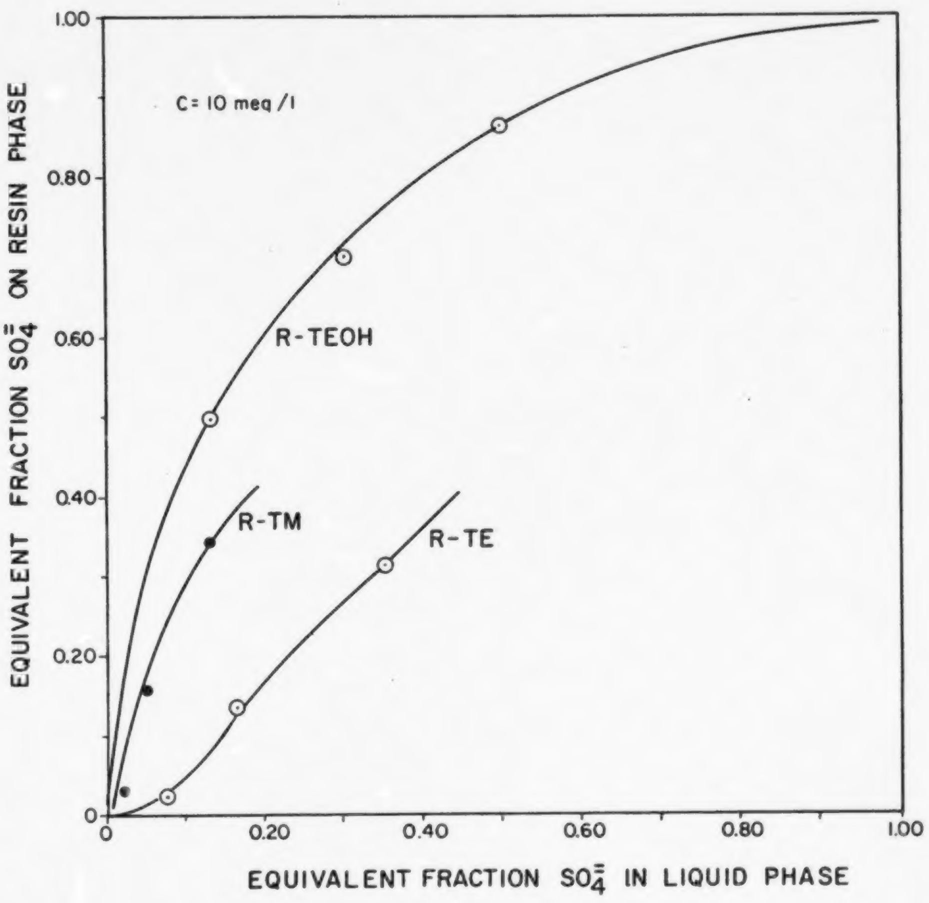
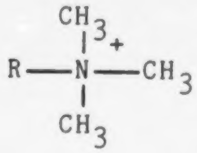
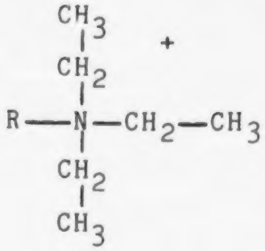
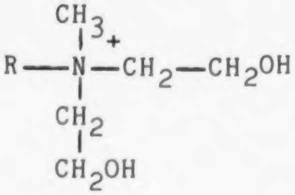


FIGURE 48 SULFATE-NITRATE ION-EXCHANGE ISOTHERMS FOR TWO SPECIAL RESINS

TABLE 26. STRUCTURES OF SPECIAL RESINS

No.	Designation	Amine	Molecular Structure*
1	R-TM	Trimethyl	 $R-N^{+}(CH_3)_3$
2	R-TE	Triethyl	 $R-N^{+}(CH_2-CH_3)_3$
3	R-MDE	Methyldiethoxy	 $R-N^{+}(CH_3)(CH_2-CH_2OH)_2$

R denotes resin backbone structure.

TABLE 26. Continued

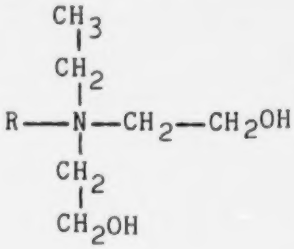
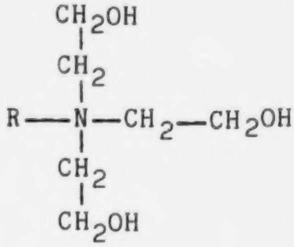
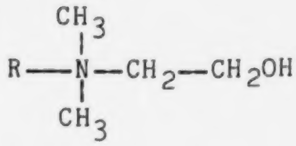
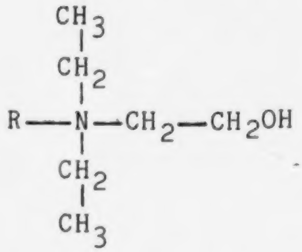
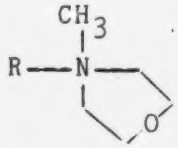
No.	Designation	Amine	Molecular Structure*
4	R-EDEOH	Ethyldiethoxy	 $R-N(CH_2CH_3)(CH_2CH_2OH)-CH_2-CH_2OH$
5	R-TEOH	Triethoxy	 $R-N(CH_2CH_2OH)(CH_2CH_2OH)-CH_2-CH_2OH$
6	R-DMEOH (same as A-104)	Dimethylethoxy	 $R-N(CH_3)(CH_3)-CH_2-CH_2OH$
7	R-DEEOH	Diethylethoxy	 $R-N(CH_2CH_3)(CH_2CH_3)-CH_2-CH_2OH$
8	R-N-MM	N-methyl-morpholine	

TABLE 27. PROPERTIES OF SPECIAL RESINS[1]

No. and Designation		Moisture[2] Content (%)	Vol. Capacity[2] (eq/l)	K_S^N (approximate)	NSS
1	R-TM	51.0	1.41	100	-0.14
2	R-TE	47.9	1.19	1,000	+0.92
3	R-MDEOH	41.1	1.41	10	-1.15
4	R-EDEOH	38.9	1.30	50	-0.41
5	R-TEOH	33.1	1.23	10	-1.09
6	R-DMEOH[3]	45.7	1.42	50	-0.45
7	R-DEEOH	43.5	1.29	100	-0.11
8	R-N-MM	44.6	1.35	200	+0.17
(Duolite	A-101D)	(48 to 55)	(1.3)	(25)	-0.71

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[1] All resins synthesized from the resin intermediate used in commercial manufacture of Duolite A-104.

[2] Data supplied by Diamond Shamrock.

[3] Same as Duolite A-104.

Two resins show positive NSS values indicating they are nitrate selective. R-TE resin shows highest nitrate-to-sulfate selectivity with R-MDEOH and R-TEOH showing least with R-TM closer to the lowest values. The K_S^N values and isotherms show outstanding dependence on chemical structures. Figure 47 also gives visual evidence of strong nitrate selectivity for R-TE which would also be evident in column performance at this concentration. These figures also show the electroselectivity effect which enhances sulfate selectivity at the lower of the two anion concentrations. Figure 47 shows the tendency of strong-base resins to have enhanced nitrate selectivity at high X_S values. Figure 48 shows that R-TE has nitrate selectivity even at the lower X_S value.

The structure effect on nitrate-to-sulfate selectivity is shown in Figure 49. Nitrate selectivity is enhanced considerably by increasing the organic material around the nitrogen atom whereas the addition of the hydroxyl groups have the opposite effect. These effects could be related to the hydrophilicity of the resin with the more hydrophobic resins having the highest affinity for the poorly hydrated nitrate. However, as shown in Table 27, R-TEOH should be the most hydrophilic but it shows the least tendency to retain moisture and R-TE should be the most hydrophobic but it contains the

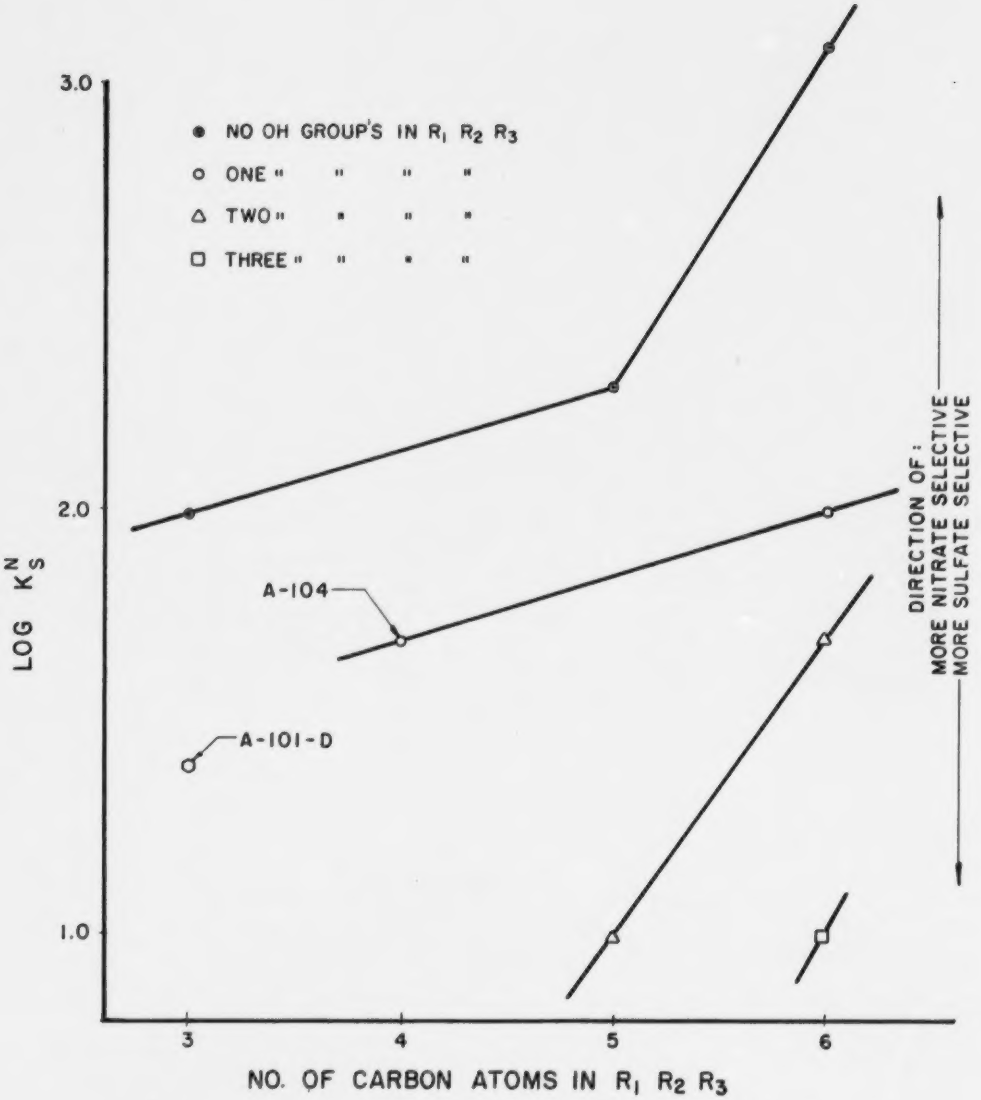
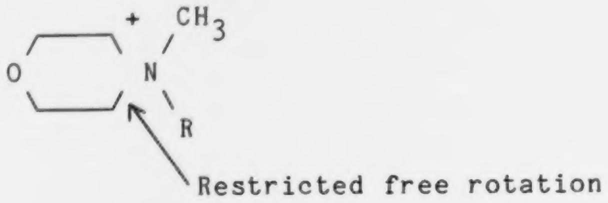


FIGURE 49 EFFECT OF STRUCTURE ON NITRATE TO SULFATE SELECTIVITY

second highest moisture content. Consequently, there may be little relationship between resin hydrophilicity and K_S^N leaving molecular structure the dominant factor.

It is postulated that the polar hydroxyl groups are able to participate in stabilizing the charge separation within the resin to some extent thereby reducing the amount of water the resin would normally require for this purpose. If this is the case, internal resin swelling strain caused by the sulfate ion is lessened by the presence of the hydroxyl groups. Any charged resin can be considered to be hydrophilic and will swell by addition of water to the extent cross linking and steric requirements will allow. The swelling will occur until internal strain equals and opposes hydration. The above postulate indicates the role of the internal hydroxyl group in this by reducing internal strain through eliminating some waters of hydration.

The role of steric hindrance around the nitrogen atom is indicated by the data in Figure 49. Only three resins were without hydroxyl groups R-TM, R-TE, and R-N-MM. The latter has a heterogeneous ring structure and was prepared as a substitute for a resin with one methyl and two ethyl groups on the nitrogen. The latter amine was unavailable. Therefore, this series of three resins does not represent a systematic variation of structure but the trend toward nitrate selectivity with increasing bulk is obvious from Figure 49; however, the value for R-N-MM is disproportionately low. The presence of the C-O-C bond in R-N-MM could have the same effect as the C-O-H bonds discussed above. An alternate explanation is that in the ring (Structure 7)



R-N-MM, Structure 7

There is less steric hindrance toward the hydrated anion than if free rotation about at least two of the C-N bonds were allowed to occur. Therefore, the steric effect is less than in a resin having one methyl and two ethyl groups. In the R-TE resin, free rotation about the three ethyl-C bonds are allowed to occur to the extent allowed by the resin structure. Three conformations of R-TE are shown in Figure 50 showing the ethyl groups in either alpha or beta positions. Conformations A and B have the least interference toward a hydrated anion. However, Conformation A is sterically strained by interference between

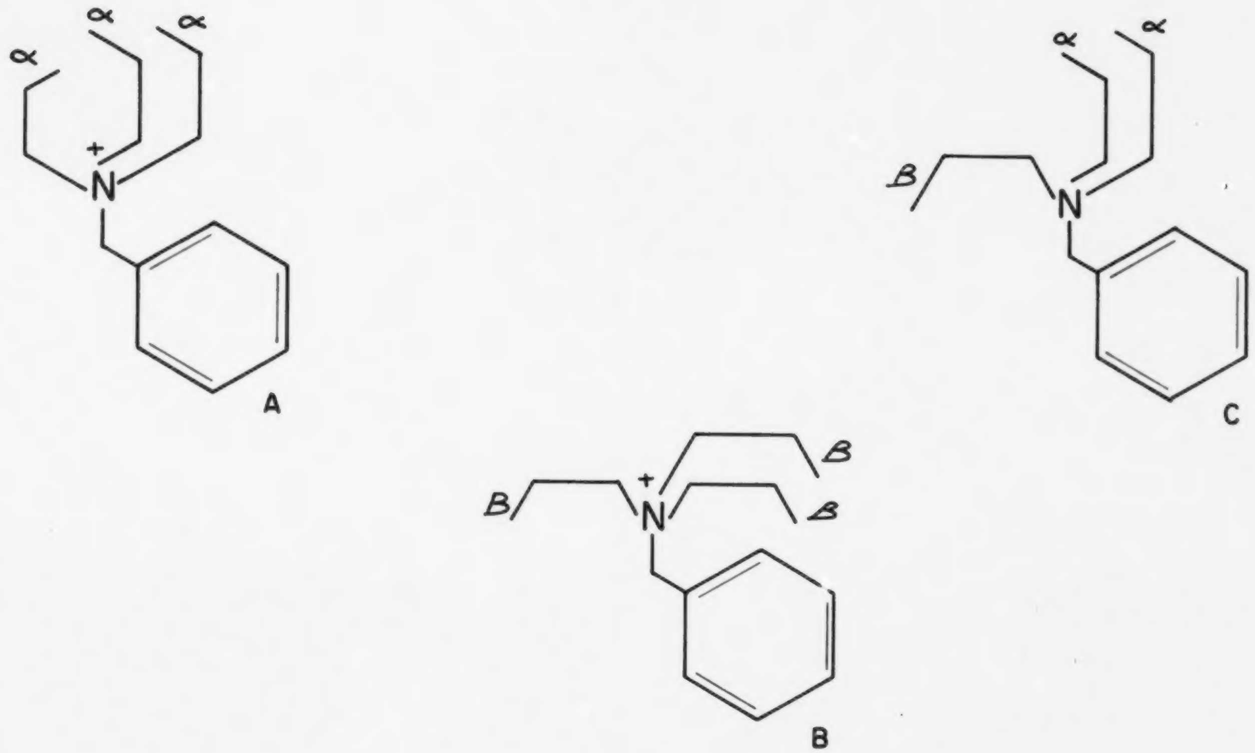

α
α
α
A
B
B
B
B
α
α
B
C

FIGURE 50 THREE CONFORMATIONS OF R-TE

the ethyl groups and Conformation B has interference between the aromatic ring and two of the ethyls in the beta position. Construction of a molecular model with Van der Waals radii is possible only for Conformation C with one ethyl group in the beta position and two in the alpha position. Strains still exist in the model which shows a well shielded nitrogen atom. Figure 51 is a photograph of the R-TE and R-TM resins showing an "anion's eye view" of the difference in structure about the nitrogen atom.

The literature of physical organic chemistry has several examples of steric effects in equilibrated systems (Reference 27). In a discussion on steric effects studied by H. C. Brown and coworkers, Hammond states ". . . none are more intriguing than the special effects of ethyl groups when they are introduced into the ammonia structure." One example given is the decrease in basicity toward trimethyl boron in the series ethyl amine, diethyl amine, triethyl amine. If, however, the ethyl groups are forced back away from the nitrogen in a cyclic amine basicity is increased. It is held that these data indicate that one of the ethyl groups in triethylamine is held in a configuration protruding in front of the nitrogen similar to Conformation C.

Nitrate-to-Chloride Selectivity

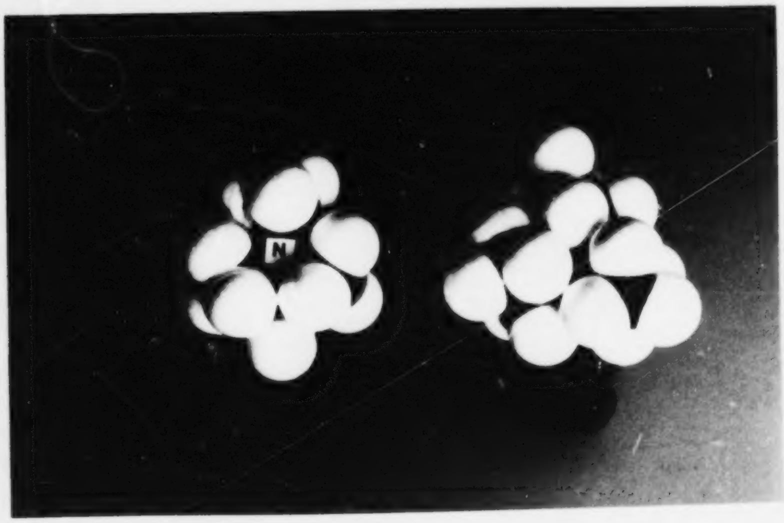
Nitrate-to-chloride selectivity constants, K_C^N, were measured for three of the resins by the vendor. The values are

R-TM	3.0
R-N-MM	4.1
R-TE	4 to 6

The R-TE resin shows a variation with the K_C^N value tending to have a maximum in the middle range of $\overline{X}_N$. This conclusion is based on a few data points and will be checked in future work. Because anion resins in the chloride form are swollen more than nitrate (and less than the sulfate form) an increase in K_C^N would be expected as steric requirements around the nitrogen increase. The presence of the maximum in K_C^N as $\overline{X}_N$ increases from 0 to 1 might be indicative of nitrate relieving steric strain as it replaces chloride up to a certain $\overline{X}_N$ with further displacement of chloride by nitrate causing a "negative strain" in the resin structure.

The structural change from R-TM to R-TE has at the most doubled K_C^N whereas K_S^N has increased tenfold. The significance of this can be realized by comparing nitrate loadings for two different solutions, one a chloride, the other a sulfate, but each having the same nitrate concentrations (X_N = .5 in each case). If

$$K_C^N = 3$$



R-TM R-TE

FIGURE 51 MOLECULAR MODELS OF RESIN STRUCTURES

$X_N = 0.5 = X_C$

$\overline{X_N}$ will be 0.600

If $K_C^N = 6$

$X_N = 0.5 = X_C$

$\overline{X_N}$ will be 0.75

The structural change has increased $\overline{X_N}$ by 0.15 units.

If $K_S^N = 100$

$X_N = 0.5 = X_S$; $C = 10$ meq/l

$\overline{C} = 1{,}200$ meq/l

$\overline{X_N}$ will be 0.46

If $K_S^N = 1{,}000$

$X_N = 0.5 = X_S$; $C = 10$ meq/l

$\overline{C} = 1{,}200$ meq/l

$\overline{X_N}$ will be 0.83

The structural change has increased $\overline{X_N}$ by 0.37 units. The general effect has been to increase the effectiveness of the resin to remove nitrate from a sulfate solution more than its effectiveness to remove nitrate from a chloride solution.

The chloride-to-sulfate selectivity constants can be estimated since

$$K_S^C = \frac{K_S^N}{K_C^N}$$

The values are

K_S^C for R-TM = 33

K_S^C for R-TE = 167

The structural change represents a fivefold increase whereas a tenfold increase was noted for the K_S^N values. It is also obvious that K_S^C for R-TE gives the resin chloride-to-sulfate selectivity in water with sulfate plus chloride of 5 meq/l or greater.

Column Tests

Several column tests were made with the special resins using Well 3 water and the procedure described in Section 4 above. These resins were all supplied in the chloride form. The conditions of comparative column tests are given in Table 28 and breakthrough curves are given in Figures 52 through 59. These curves were obtained using either completely regenerated or virgin resin in the chloride form. Resins are listed in Table 28 in decreasing order of K^N_S values except for A-101D which is given as a reference. The breakthrough curves show the definite effect of the structural changes. Figure 52 for R-TE shows early breakthrough for sulfate which rapidly rises to a value exceeding its influent concentration and a much delayed nitrate breakthrough. The curve for A-101D is given as a reference and shows the extended bed life for the R-TE resin over A-101D to be a factor of 275/170 or 1.62, although R-TE has 92 percent of the capacity of the A-101D. The respective $\overline{X}_N$ values are 0.28 and 0.15. The curve for R-N-MM shows similar characteristics but less BV(N) and greater BV(S) than for R-TE. The curve for R-TM shows a continuing trend with nitrate selectivity characteristics nearly vanished. The curve for R-DEEOH reverses the trend and shows stronger nitrate selectivity characteristics than exhibited by R-TM. The remainder of the resins show a trend toward sulfate selectivity with the R-TEOH showing the obvious characteristics with prior nitrate breakthrough. The breakthrough curves show greater differences between the resins than expected from their K^N_S values. This is particularly noted in the case of R-DEEOH which shows a breakthrough curve with higher nitrate selectivity and bed life than R-N-MM although both K^N_S (from equilibrium) and C are lower for R-DEEOH. R-MDEOH (Figure 58) does not show the enhanced nitrate effluent even though K^N_S is very low. The K^N_S (equilibrium) values were measured at 50 meq/l total anion concentrations and columns were operated at about 8.5 meq/l. It is known that concentration does influence K^N_S because of changes in activity coefficients of ions and resin. K^N_S values can be estimated from the column data for four of the resins by assuming these resins are 100 percent loaded with nitrate and sulfate at the nitrate breakthrough and are in equilibrium with the incoming nitrate and sulfate ions. These K^N_S (column) values are given in Table 28. For R-TE, a decrease has occurred whereas an increase has occurred for the other three resins. One major difference between column and equilibrium data is one of possible kinetic effects in the column data, i.e., the column may not be in equilibrium with feedwater. If kinetic effects are responsible for these differences they favor higher K^N_S in three of the four resins which offset any decrease in K^N_S which may be due to concentration effects (lower total anion concentrations generally favoring lower resin selectivity differences). These data support the observed tendency (see Section 6) of high flow rates to favor nitrate selectivity.

TABLE 28. CONDITIONS OF COMPARATIVE COLUMN TESTS

Run No.	Resin	meq/l Nitrate	meq/l Sulfate	BV(S)	BV(N)	Figure	K_S^N From Data Equilibrium*	K_S^N From Data Column
08140	A-101D	1.14	7.25	185	170	52	25	---
08150	R-TE	1.21	7.50	135	275	52	1,000	653
09290	R-N-MM	1.32	7.75	170	225	53	200	350
10020	R-TM	1.33	7.75	178	195	54	100	232
10300	R-DEEOH	1.25	6.67	170	230	55	100	332
11140	R-DMEOH	1.22	7.17	200	190	56	50	
10200	R-EDEOH	1.24	6.50	185	160	57	50	
11060	R-MDEOH	1.13	7.50	220	175	58	10	
10130	R-TEOH	1.24	6.67	175	135	59	10	

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*Measured at nitrate + sulfate = 50 meq/l.

Note: Chloride average = 2.63 meq/l; bicarbonate average = 1.46 meq/l.
Flow rate = 0.33 BV per minute.

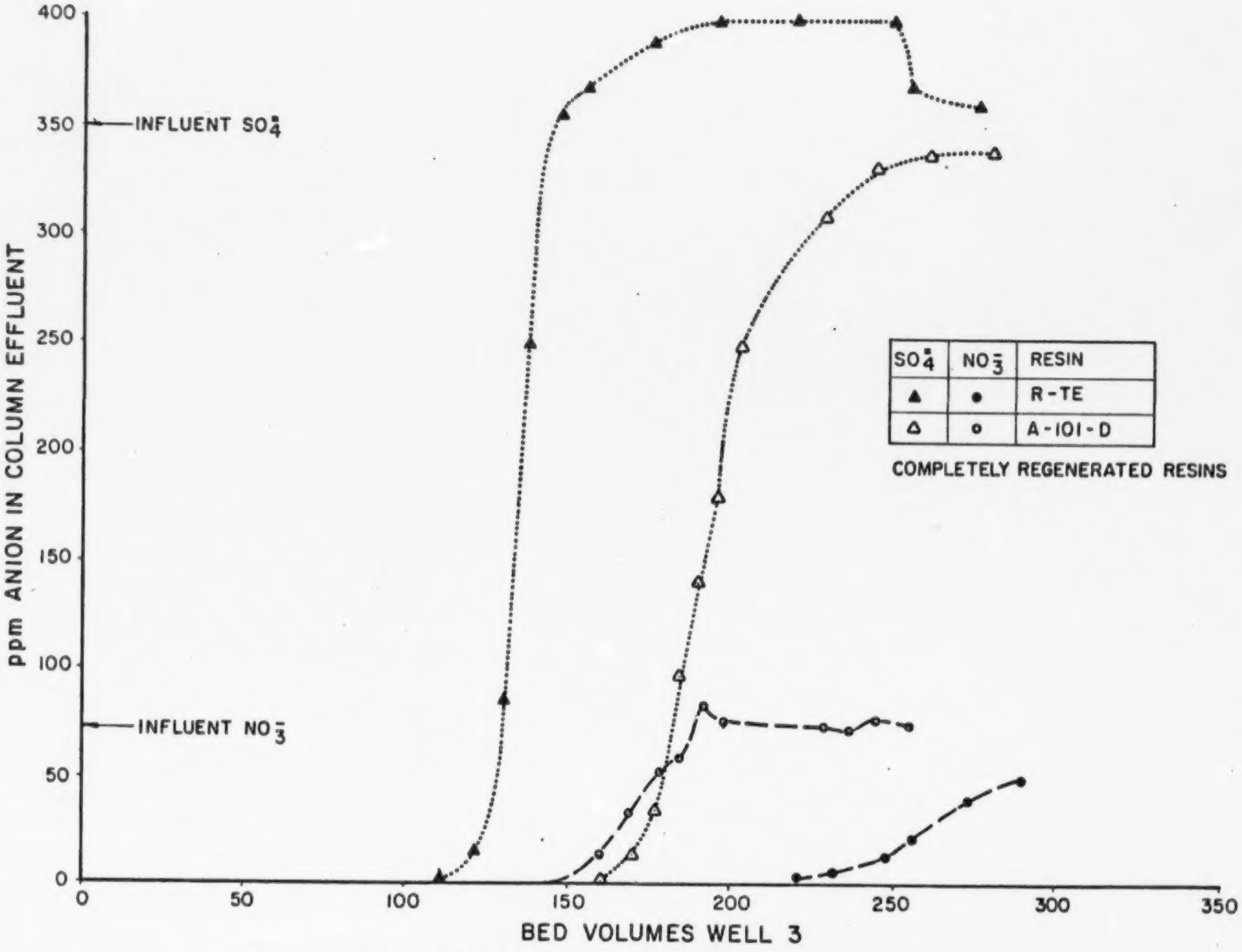

FIGURE 52 ION EXCHANGE COLUMN EXPERIMENT 08140 & 08150

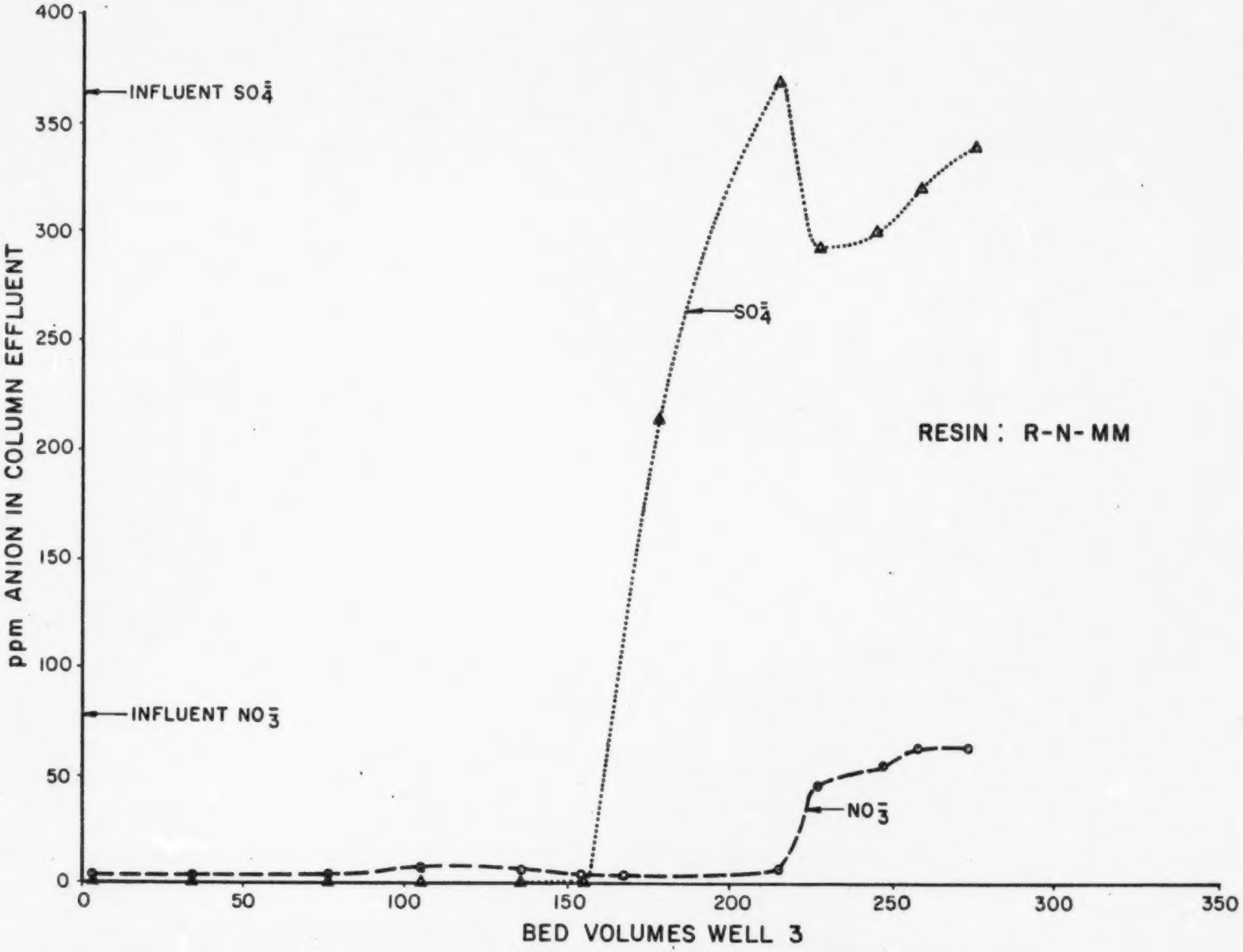

FIGURE 53 ION EXCHANGE COLUMN EXPERIMENT 09290

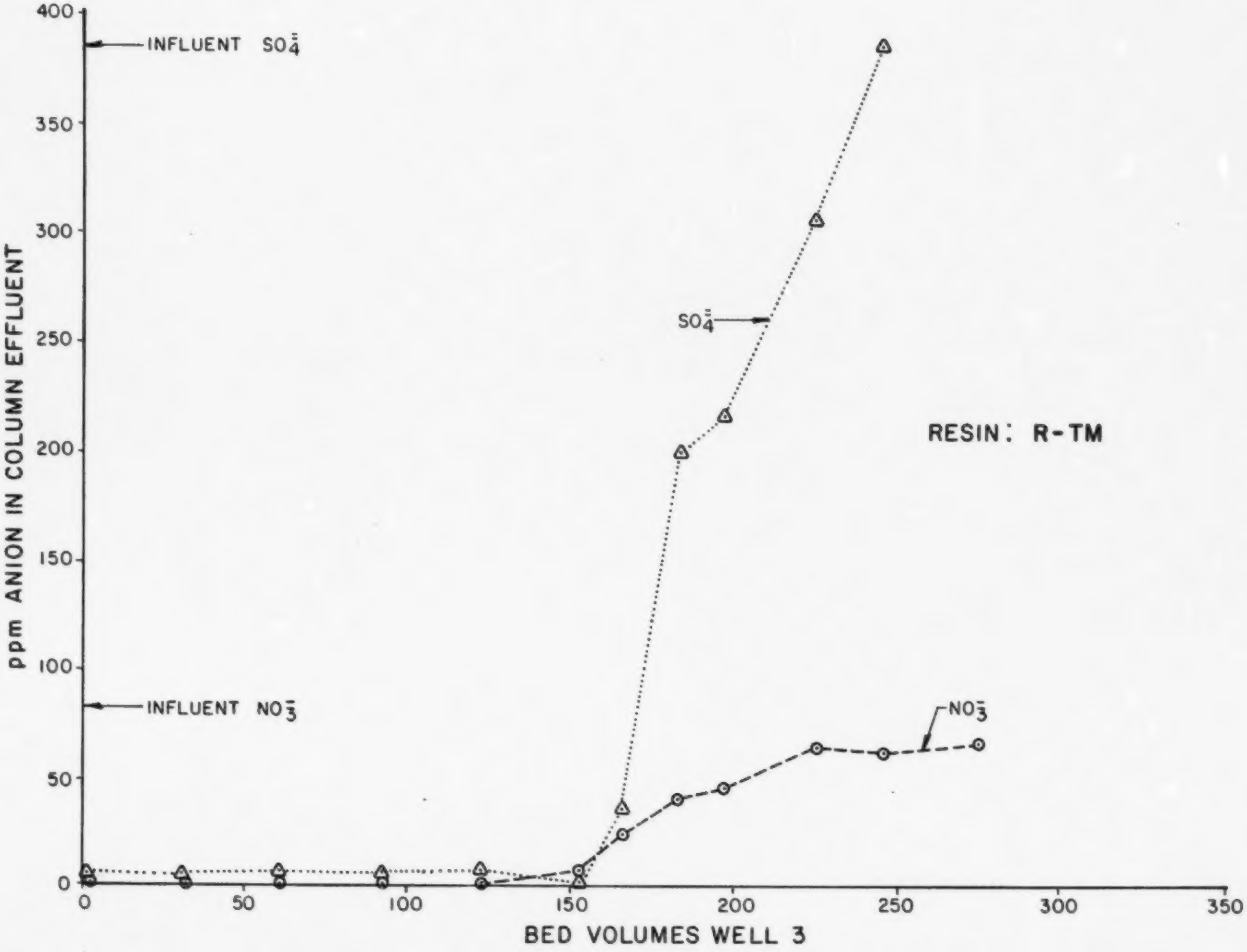

FIGURE 54 ION EXCHANGE COLUMN EXPERIMENT 10020

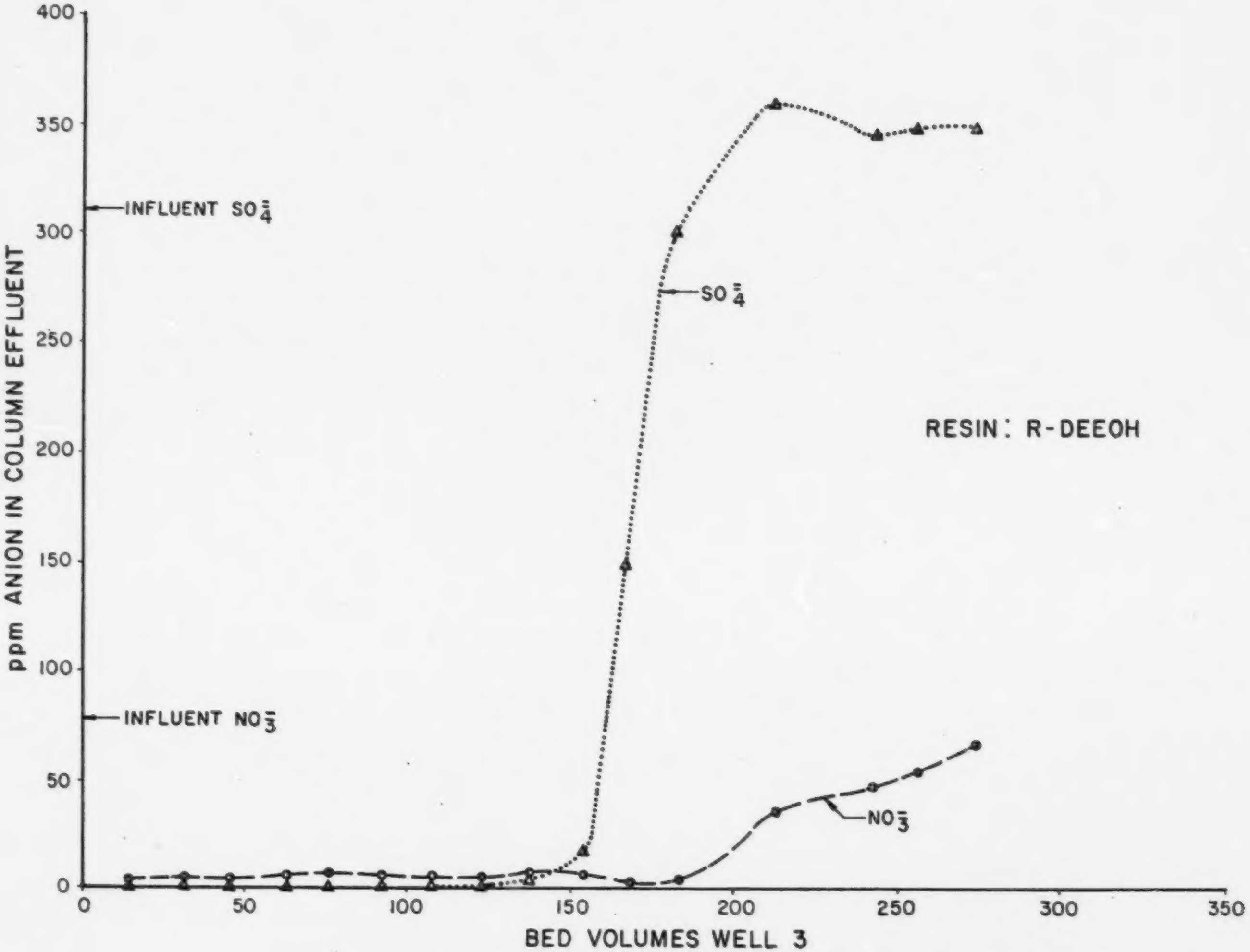

FIGURE 55 ION EXCHANGE COLUMN EXPERIMENT 10300

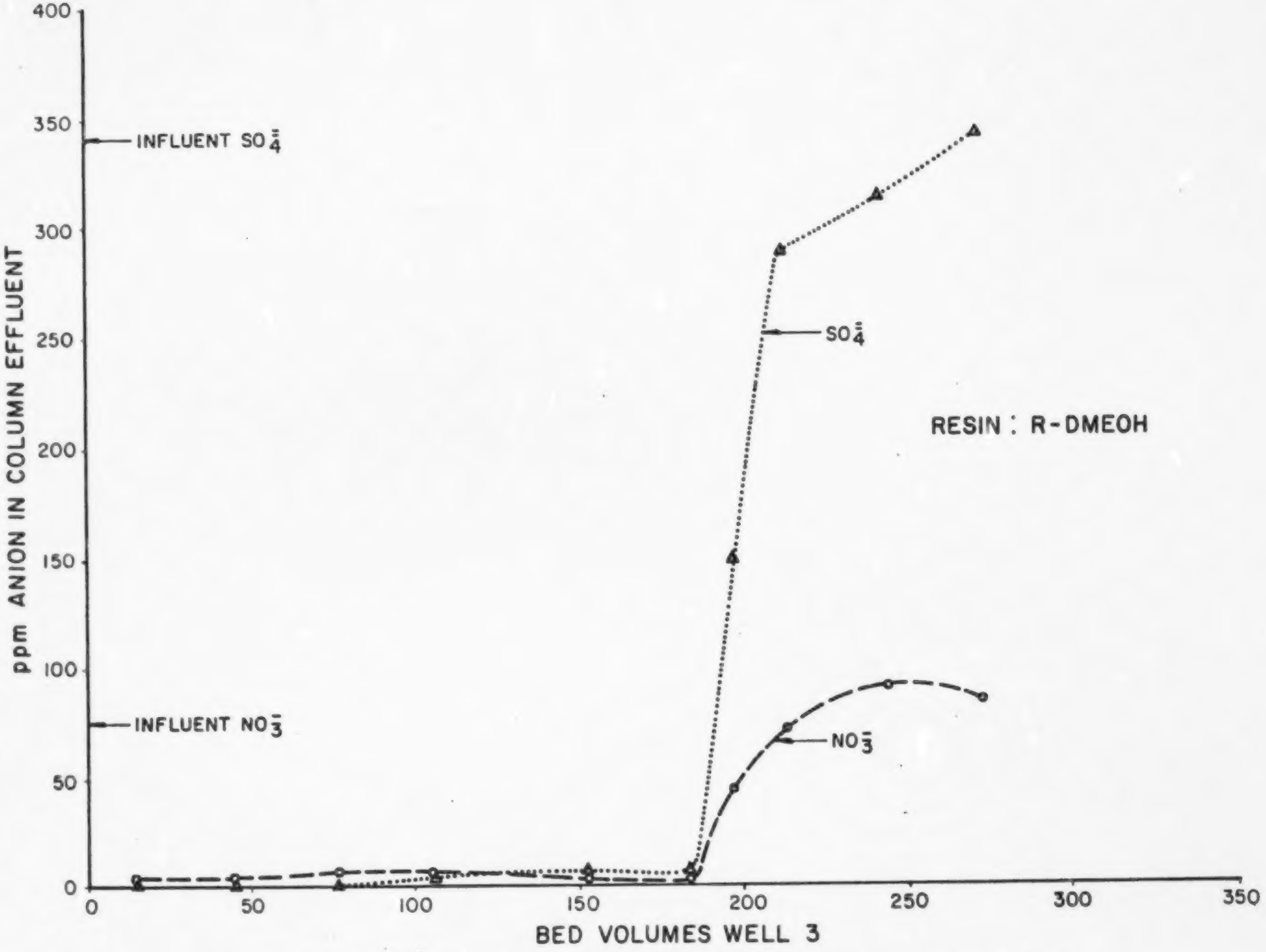

FIGURE 56 ION EXCHANGE COLUMN EXPERIMENT 11140

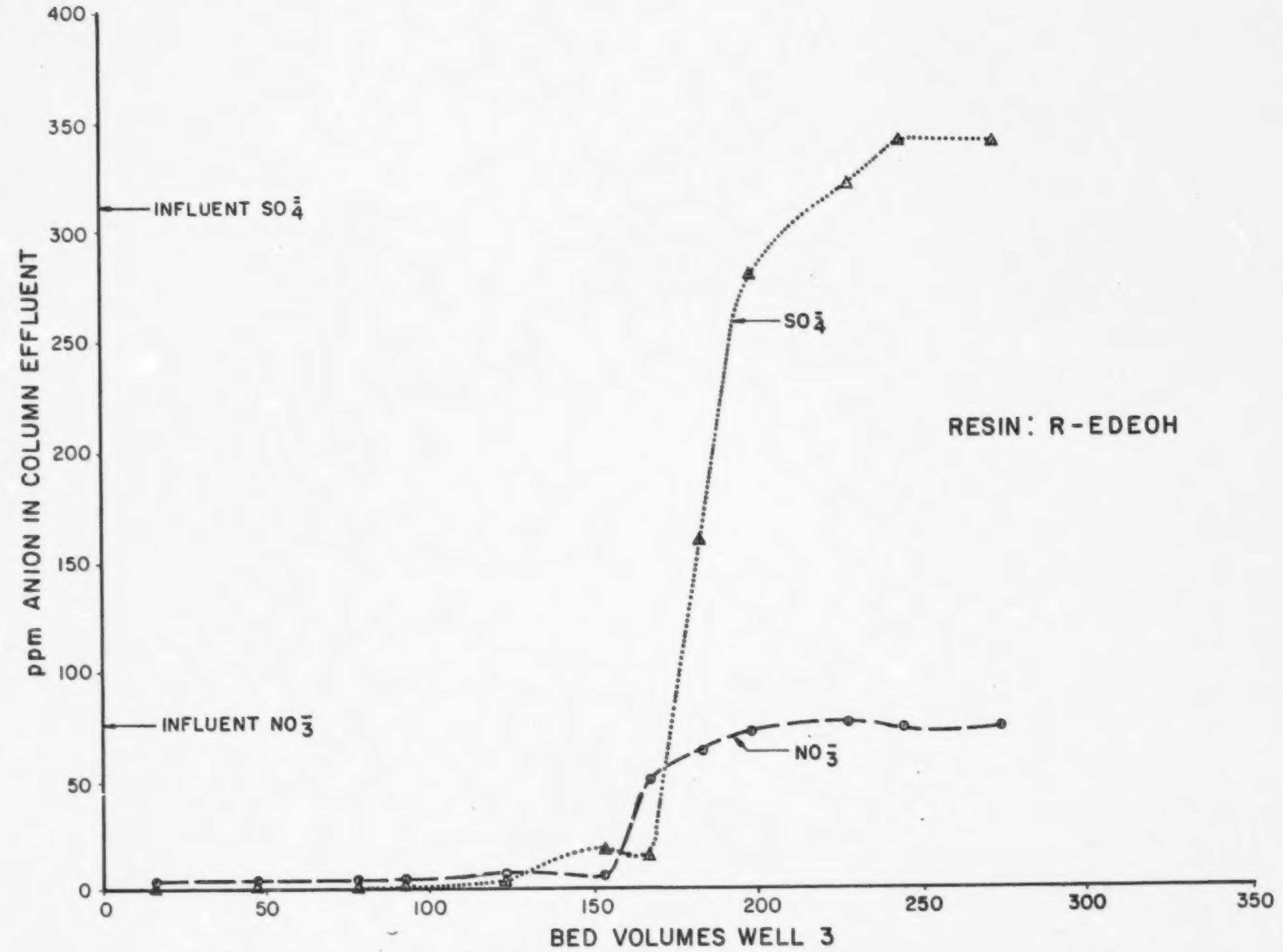

FIGURE 57 ION EXCHANGE COLUMN EXPERIMENT 10200

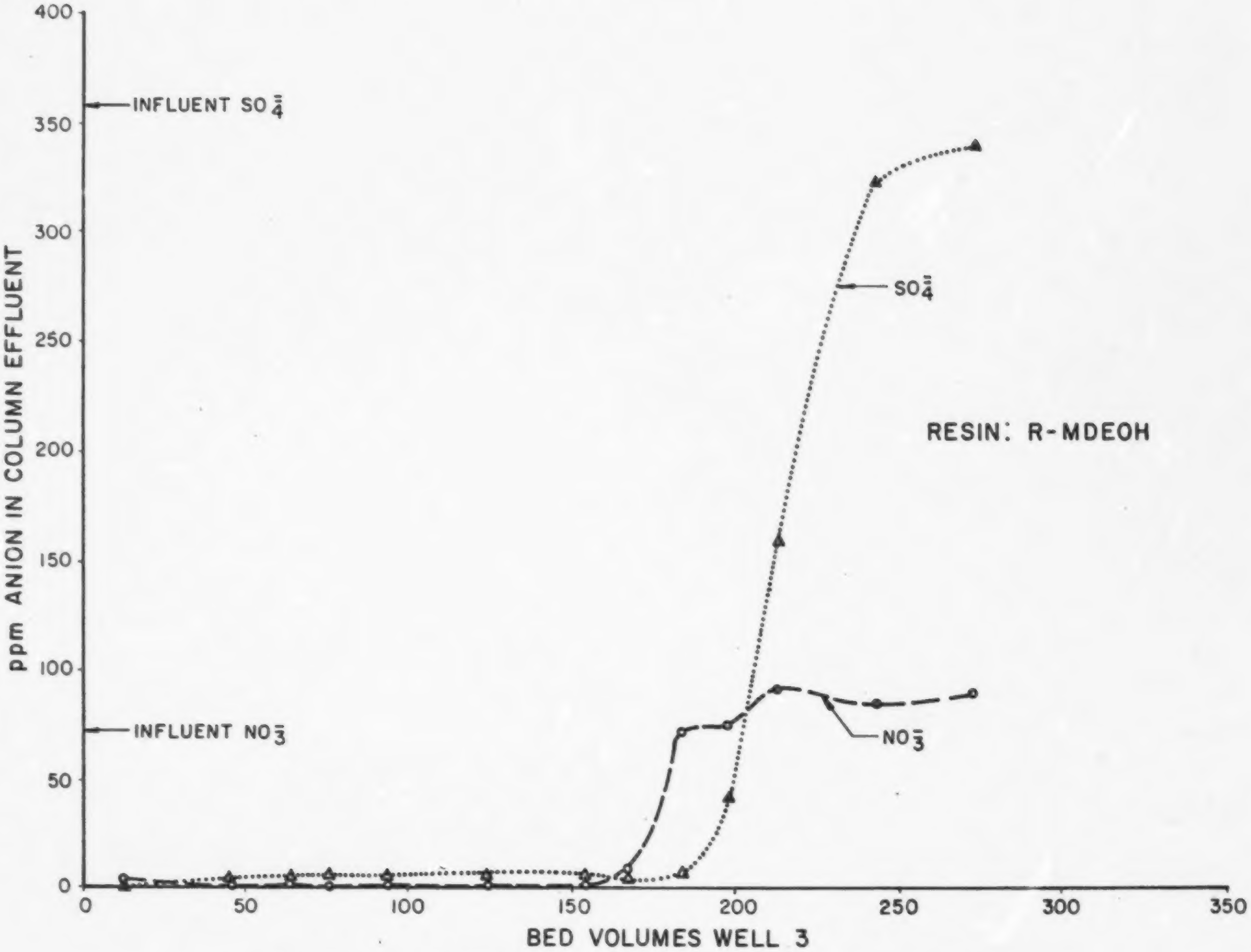

FIGURE 58 ION EXCHANGE COLUMN EXPERIMENT 11060

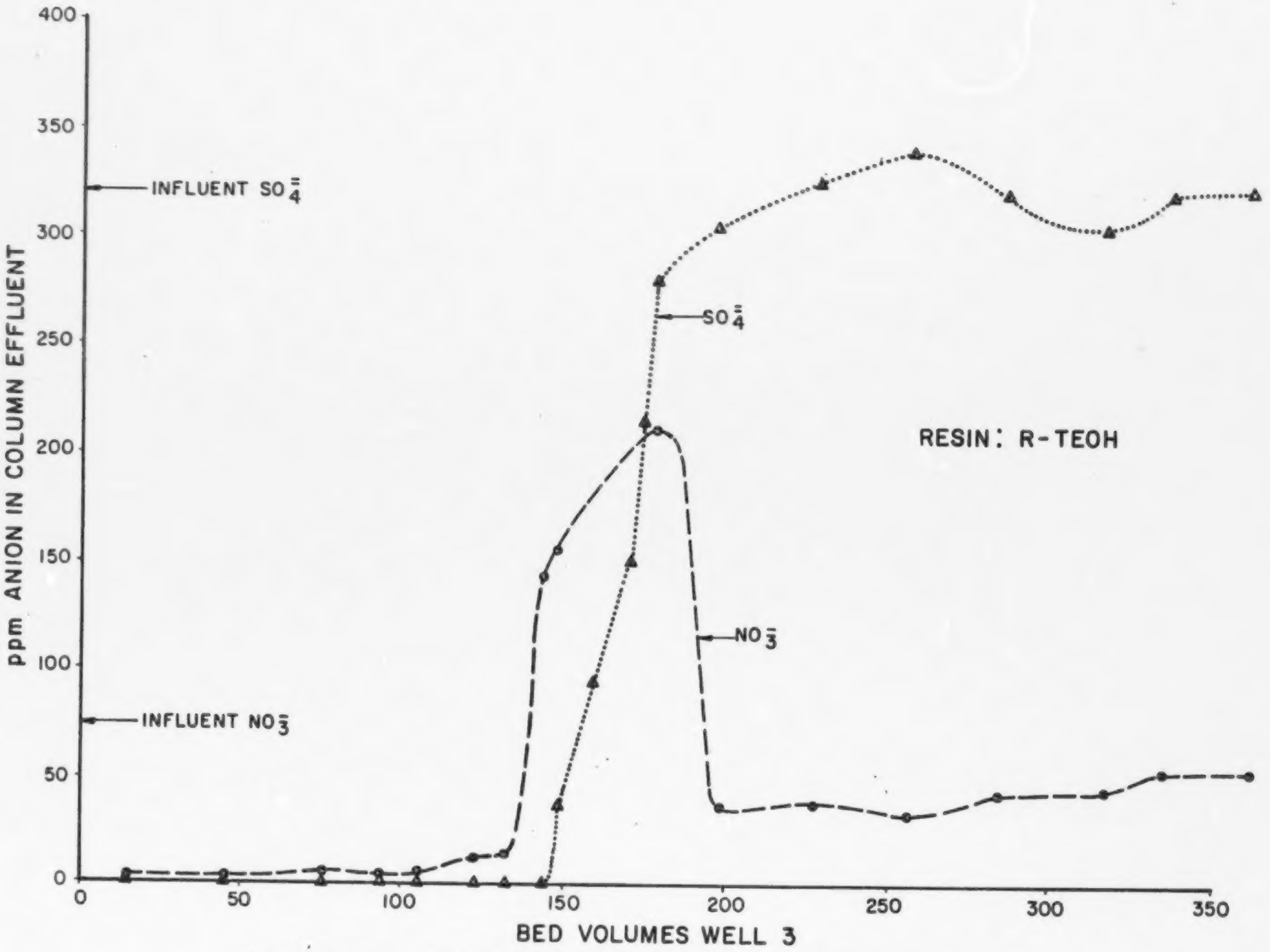

FIGURE 59 ION EXCHANGE COLUMN EXPERIMENT 10130

The curve for R-TEOH resin shows definite kinetic effects operating since nitrate levels remain well below the influent value for several bed volumes beyond nitrate breakthrough indicating that complete sulfate absorption by the resin takes place slowly. It was postulated in the above discussion on structural effects on K_S^N that the presence of C-O-C or C-O-H bonds in the resin enhances sulfate selectivity by reducing the hydration requirements of the resin sulfate salt and reducing resin strain. Because of possible restriction of rapid changes in C-O and O-H bond angles within the resin, the sulfate absorption may be slower than nitrate giving rise to the observed kinetic effects. A major advantage of R-TE resin is the slow rise in the nitrate breakthrough and the absence of the enhanced nitrate concentration in the effluent making process control less critical.

REGENERATION EXPERIMENTS

Comparison of A-101D and R-TE

Utility of a nitrate-selective resin must necessarily consider regeneration of the resin into the chloride form. That the special resins are indeed regenerable can be seen from the fact that the structural changes have less influence on K_C^N than on K_S^N and K_C^N remained fairly low. Regeneration experiments were conducted using column tests at various levels of regeneration. Side-by-side column runs were made with A-101D and the special resins. Figure 60 gives a typical pair of breakthrough curves obtained on Well 3 water using 4 BV of 6 percent brine as regenerant. Initial nitrate leakages are about 10 to 15 ppm for each. After sulfate breakthrough, the R-TE column's nitrate leakage rises gradually to 45-ppm nitrate at BV(N) of 280. The average nitrate leakage was 21 ppm. Thus, 271 meq of nitrate were removed per liter of R-TE resin. If the column is allowed to continue to remove nitrate to 395 BV, the average nitrate leakage would be 33 ppm by blending first and last halves of the run. In this case, 306 meq of nitrate are removed per liter of resin. Comparing this to the performance of A-101D, an average nitrate leakage of 16 ppm was obtained up to the BV(N) of 175 bed volumes at 45-ppm nitrate. Thus, 183 meq of nitrate were removed per liter of A-101D. The ratio of 271/183 and 306/183 represents a 48 and 67 percent increase in regeneration efficiency. This can be further improved by extending the run to higher levels of average nitrate leakage or until leakage equals influent level. This is estimated as 420 BV to give an average nitrate leakage of 34 ppm. Nitrate removed would be 318 meq/l of resin or 73 percent more nitrate removal than obtained with A-101D using the same amount of regenerant.

The average nitrate leakage for A-101D is lower than for R-TE. This is to be expected because R-TE has more nitrate to be removed being more fully loaded with nitrate. However, R-TE

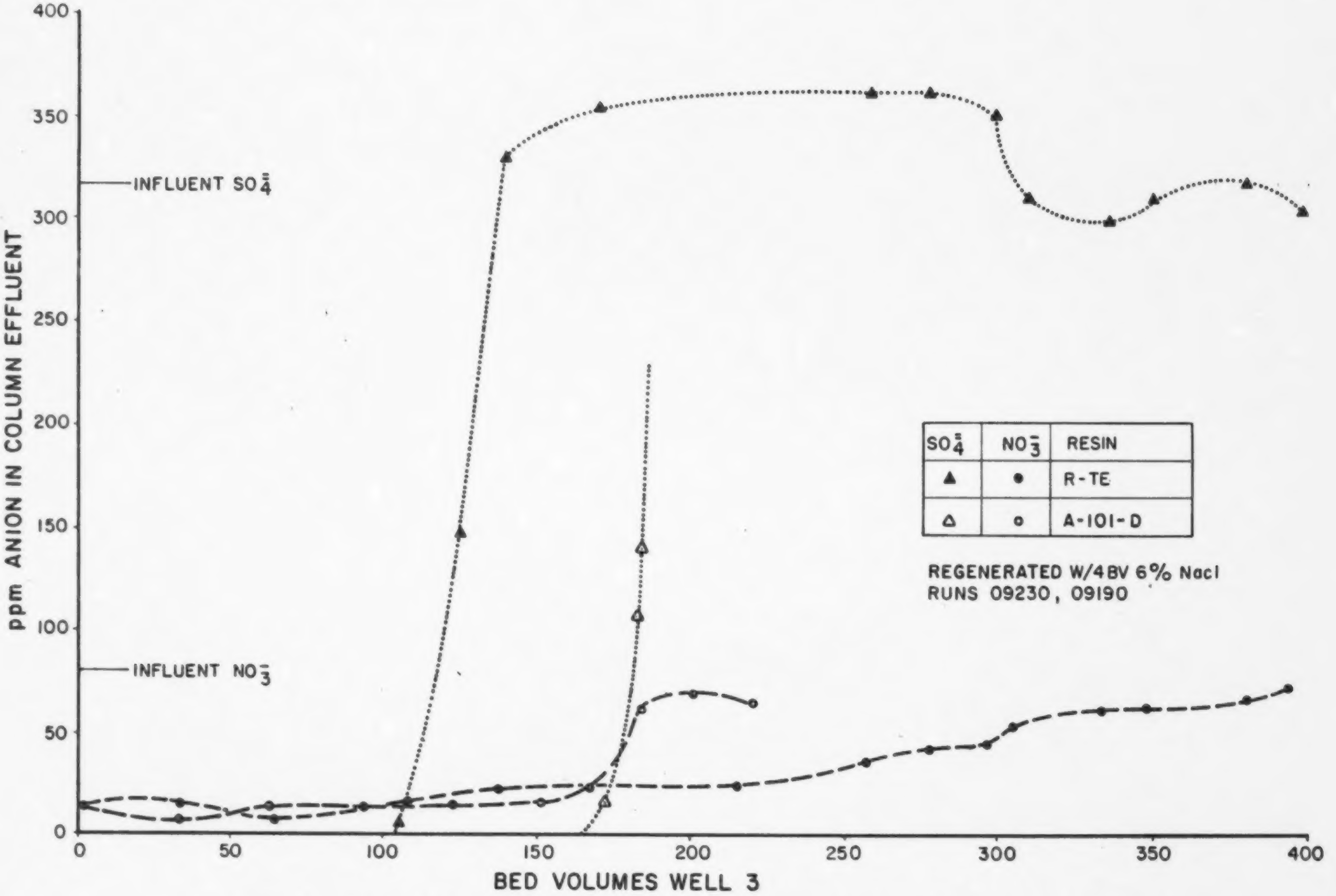

FIGURE 60 ION EXCHANGE COLUMN EXPERIMENT 09230 & 09190

has less sulfate making more regenerant available for chloride removal. The net effect is higher nitrate removal with the R-TE resin per pound of regenerant.

The use of R-TE provides two options when operating the column in the partial regeneration mode because of the slow rise in nitrate leakage: either operate to 45-ppm leakage or extend operation beyond this point while the column can still remove nitrate to the point where influent nitrate equals leakage. This would require blending first and last halves of the run to obtain an average nitrate leakage. The major advantage of this extended operation of the column is to take advantage of the high nitrate capacity of the column in this mode. Comparison of the regeneration efficiency using A-101D and using R-TE in the extended mode are given in the following section.

Partial Regeneration

A series of 21 column runs was made with the two resins comparing performances at different levels of partial regeneration. These experiments were done because loss in regeneration efficiency at higher levels of regeneration makes it desirable to operate the columns at the lowest level of regeneration possible. The data is given in Table 29.

The amounts of nitrate removed by a quantity of resin per BV of regenerant for each column run is plotted versus BV of 6 percent regenerant in Figure 61. Each curve must pass through the origin. Two curves are plotted for R-TE although all runs were continued to well past the 45-ppm breakthrough point. Consequently, somewhat better performance would be expected from R-TE at high levels of regeneration if the runs had been terminated at 45 ppm. As can be seen in Figure 61, the R-TE-45 curve shows low regeneration efficiency at low levels of regeneration. At these levels, after regeneration the column contains about as much nitrate as the A-101D as indicated by nitrate leakages; however, the bed life is much shorter (compare Runs R-42 and R-43 with R-40 and R-45). Figure 62 shows the breakthrough curve for Run R-45. A premature nitrate breakthrough occurs at 95 BV because of the high sulfate breaking through at this point. The effluent changes from a chloride-nitrate composition where monovalent-to-monovalent ion-resin equilibrium prevails to one of sulfate-nitrate composition where divalent-to-monovalent ion-resin equilibria prevails. After the sulfate break occurs, the column continues to remove nitrate for several BV.

As regeneration levels rise, breakthrough curves become more like the R-TE curve shown in Figure 60.

It can be noted here that a characteristic of R-TE is to give a slow rise in nitrate breakthrough preceded by a sharp sulfate breakthrough.

TABLE 29. DATA FOR TWO MODES OF USING R-TE

Run No.	BV 6% Brine	Influent Nitrate (ppm)	BV(N)		Average Nitrate Leakage (ppm)		meq Nitrate Removed per Liter of Resin		Resin	
			To 45 ppm	Extended	To 45 ppm	Extended	To 45 ppm	Extended	A-101D	R-TE
R	2.6	82.7	200	---	12	---	228		X	
R29	2.6	71.3	230	---	23	---	179			X
R34	1.0	70.4	106	---	38	---	56			X
R36	2.6	69.9	152	---	9	---	149		X	
R37	2.6	77.4	243	320	25	33	205	229		X
R59	4.0	81.0	280	395	21	33	271	306		X
R42	1.3	80.1	160	---	32	---	124	---	X	
R43	1.3	81.8	105	---	32	---	84	---		X
R40	1.3	80.5	152	---	35	---	111	---	X	
R45	1.3	81.0	95	365	34	56	72	147		X
R47	1.3	84.5	165	---	36	---	129	---	X	
R50	2.0	75.7	175	---	20	---	157	---	X	
R51	2.0	74.4	220	330	31	38	154	176		X
R52	2.0	73.9	160	---	19	---	142	---	X	
R54	2.6	75.7	155	---	17	---	147	---	X	
R55	2.6	75.7	220	276	24	30	183	203		X
R56	2.6	82.3	150	---	16	---	160	---	X	
R57	2.6	81.0	220	350	23	35	205	259		X
R58	4.0	81.0	175	---	16	---	183	---	X	
R59	4.0	81.0	280	420	21	34	271	318		X
561	4.0	75.7	265	364	24	25	221	298		X

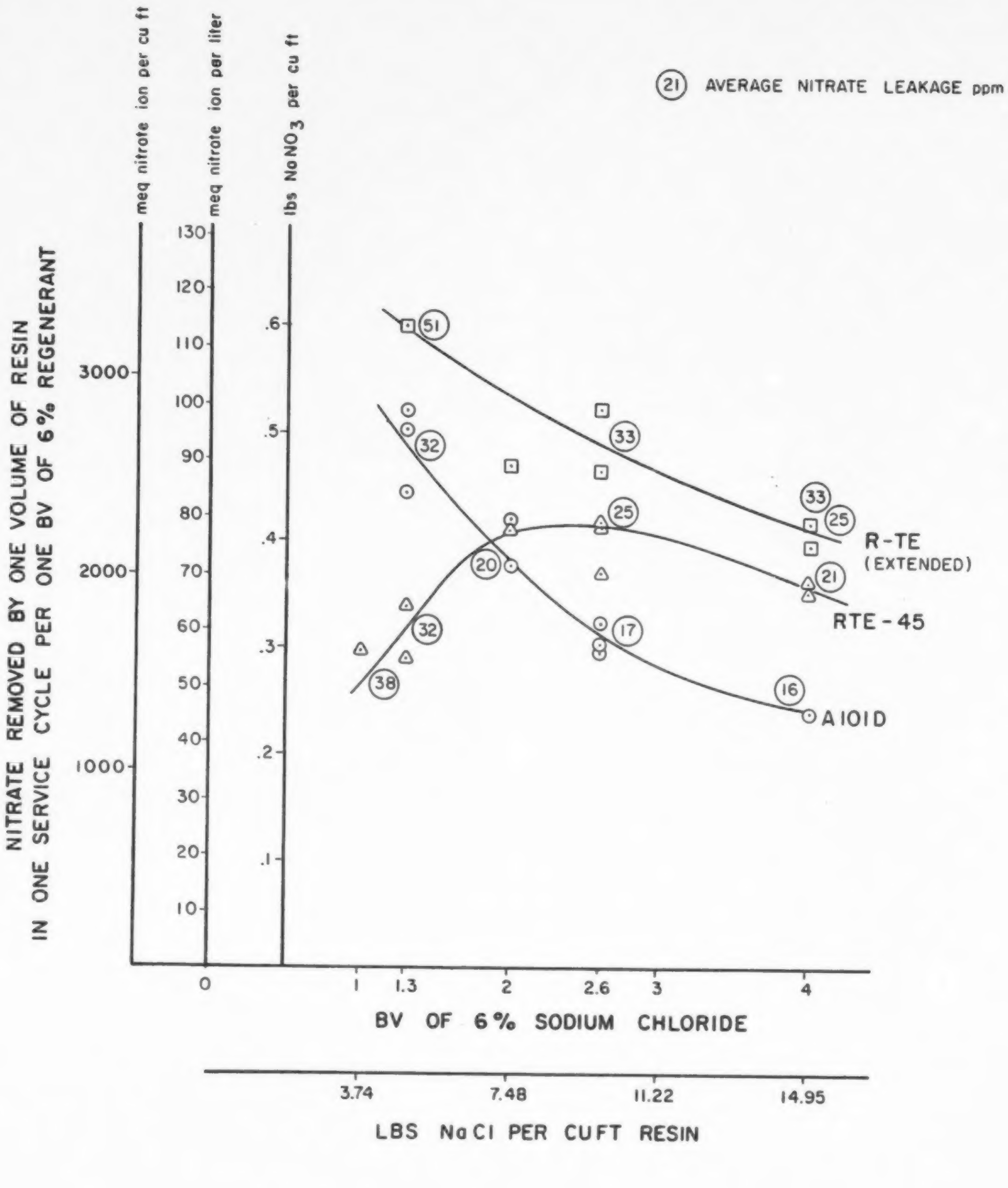

FIGURE 61 COMPARISON OF REGENERATION EFFICIENCIES

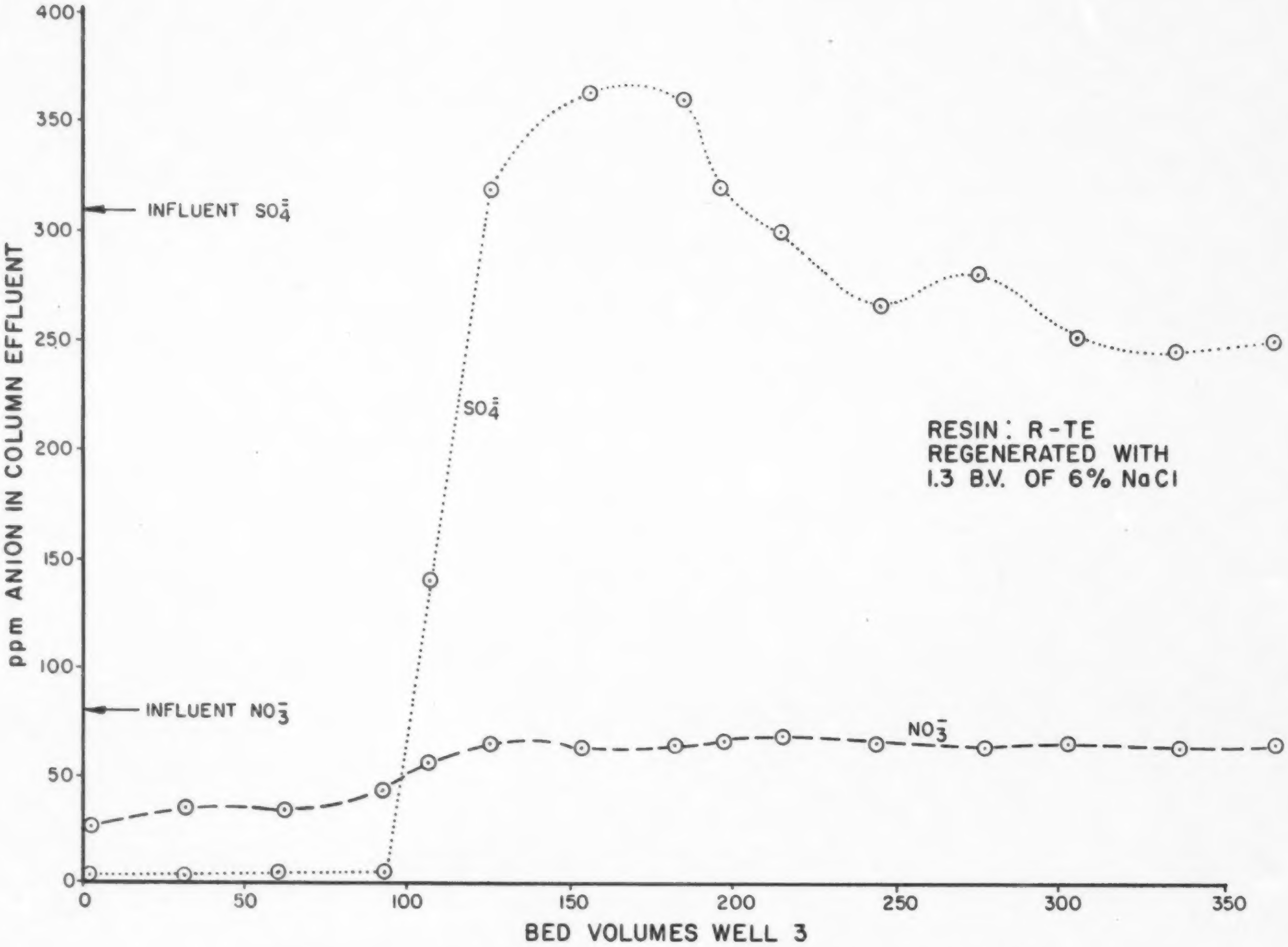

FIGURE 62 ION EXCHANGE COLUMN EXPERIMENT R-45

With a partially regenerated column, the nitrate breakthrough is compound and can take place in two steps. The first is a rather sharp rise and occurs simultaneously with sulfate breakthrough. The second is a slow rising nitrate curve with definite nonsharpening characteristics.

Bed volumes to breakthrough and nitrate leakages can be estimated for R-TE using equilibrium relationships presented in Reference 1. The second nitrate breakthrough, BV(N)-2, is estimated first for a fully regenerated column using Equation (3). C, $\overline{C}$, X_S, and K_S^N are known. For example, if $C = 8.71$, $\overline{C}$ is 1,190, X_S is 0.86, and K_S^N is 653 then at the end of the run, it is estimated that $\overline{X_N} = 0.28$.

$$BV(N)\text{-}2 = \frac{0.28 \times 1,190}{0.14 \times 8.71} = 273$$

Use of 1.3 BV of 6 percent sodium chloride will reduce $\overline{X_N}$ to approximately 0.18 (from Figure A-14, Reference 1, corrected for sulfate) and reduce resin capacity from 1,190 to 976 meq/l ($= \overline{C}'$) BV(N)'-2 for the partially regenerated column will be

$$BV(N)'\text{-}2 = 273\ (1 - .18) = 224$$

As can be seen from Figure 62, this is too low. The nitrate leakage prior to BV(N)'-2 is also estimated from Equation (3). In this case, $K = 653$, $C = 8.71$, $\overline{X_S} = 0.82$. X_N in effluent is 0.09, and nitrate leakage is 49 ppm which is in fair agreement with Figure 62.

The first nitrate breakthrough BV(N)'-1 occurs simultaneously with BV(S). If chloride and bicarbonate are negligible on the column at this point

$$BV(N)'\text{-}1 = BV(S) = \frac{C'}{C} = \frac{976}{8.71} = 112.$$

This is in good agreement with Figure 62 which shows a first nitrate break about 95 to 100 BV. The nitrate leakage prior to this point is estimated from Equation (2) of Reference (1) as 30 ppm using $C = 13$ meq/l and $K_C^N = 4$. This is in good agreement with the observed average of 34 ppm.

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APPENDIX

Sections From Reference 1

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Section 5 Results of Ion Exchange Pilot Column Tests. . . 179

References for above sections 200

NOTE: Figures A-1 through A-13 are identical to Figures 1 through 13 of Reference 1 and are deleted here.

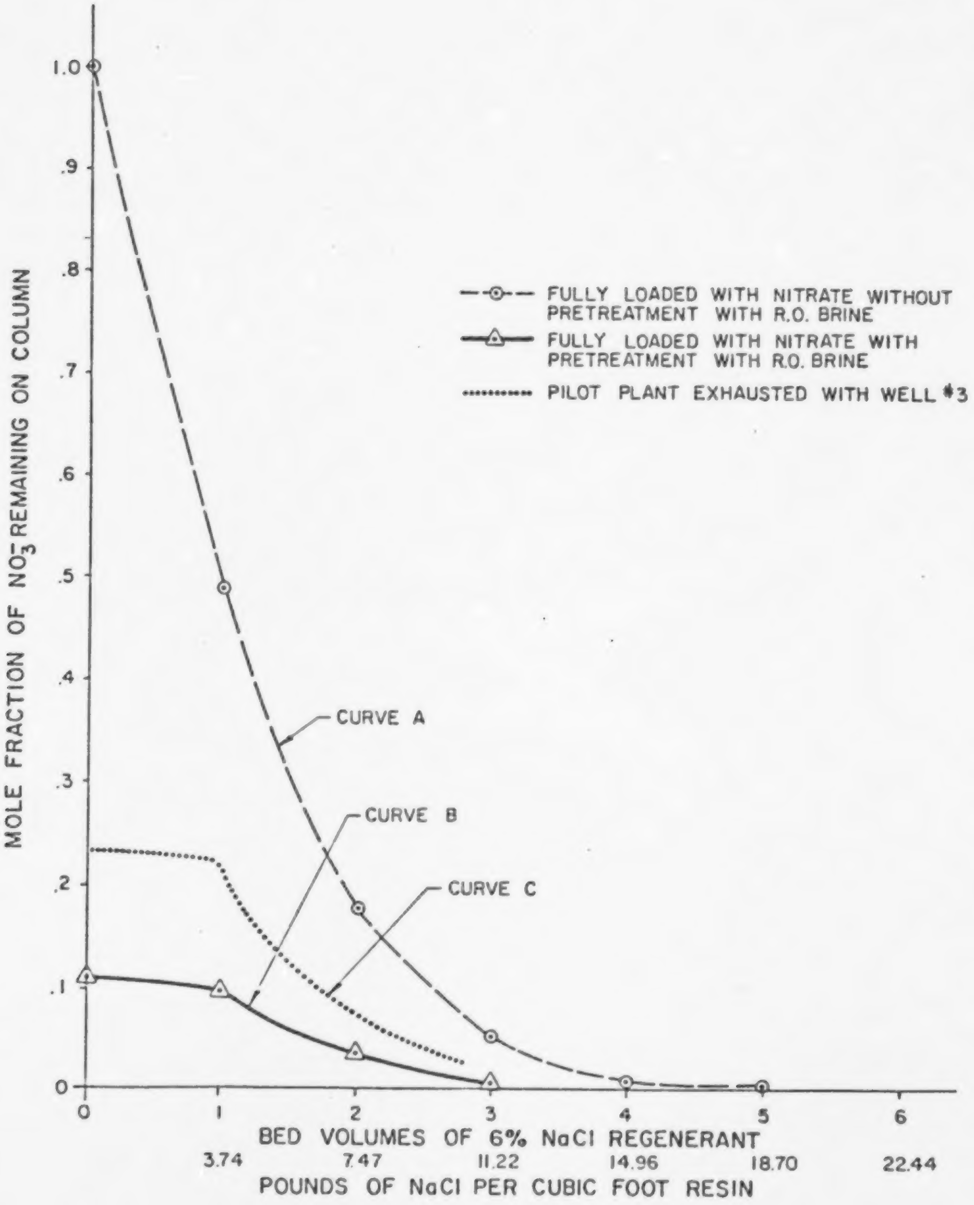


FIGURE A-14 COMPARISON OF NITRATE REMAINING ON COLUMNS DURING REGENERATION

A-1

SECTION 4

THEORETICAL CONSIDERATIONS AND DATA INTERPRETATION

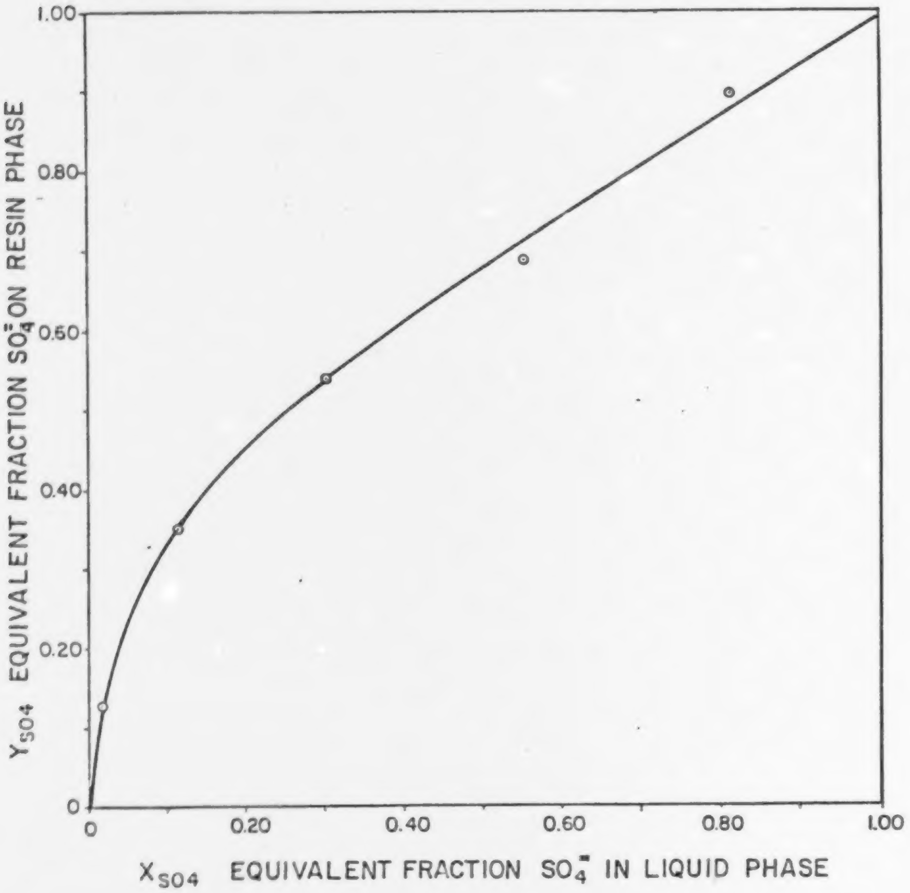
PREVIOUS WORK

The experimental work done on this program is subsequent to work done by Clifford and Weber (Reference A-2). In that effort, 32 commercially available anion resins were studied in both equilibria and laboratory column experiments. Binary isotherms were obtained under equilibrium conditions and separation factors were related to resin properties. Examples of binary isotherms are reproduced here in Figures A-15, A-16, and A-17 for the two Duolite and one Amberlite resins studied in that effort which also included chromatographic column studies at 2.5 to 5 BV per minute exhaustion rates. At these flow rates, equilibrium was achieved on the column whose performance could then be related to the isotherm data. The work of Clifford and Weber is also referred to here as an excellent general review of ion exchange materials and their use for nitrate removal. The primary thrust of the work was to study ion exchangers for the purpose of comparing a single-bed process to a two-bed process. Important parameters, such as flow rate and resin regeneration aspects of either process, were thus not studied for optimum performance. The work was also limited to water of a single composition and thus not directly applicable to well water found in McFarland, California. Frequent reference to the Clifford and Weber work will be made throughout this discussion. Important conclusions drawn by Clifford and Weber, which are pertinent to this work, are those relating to the selectivity that all anion exchange resins tested show for sulfate over nitrate ion and the resin properties influencing that selectivity.

RESIN-ION EQUILIBRIA

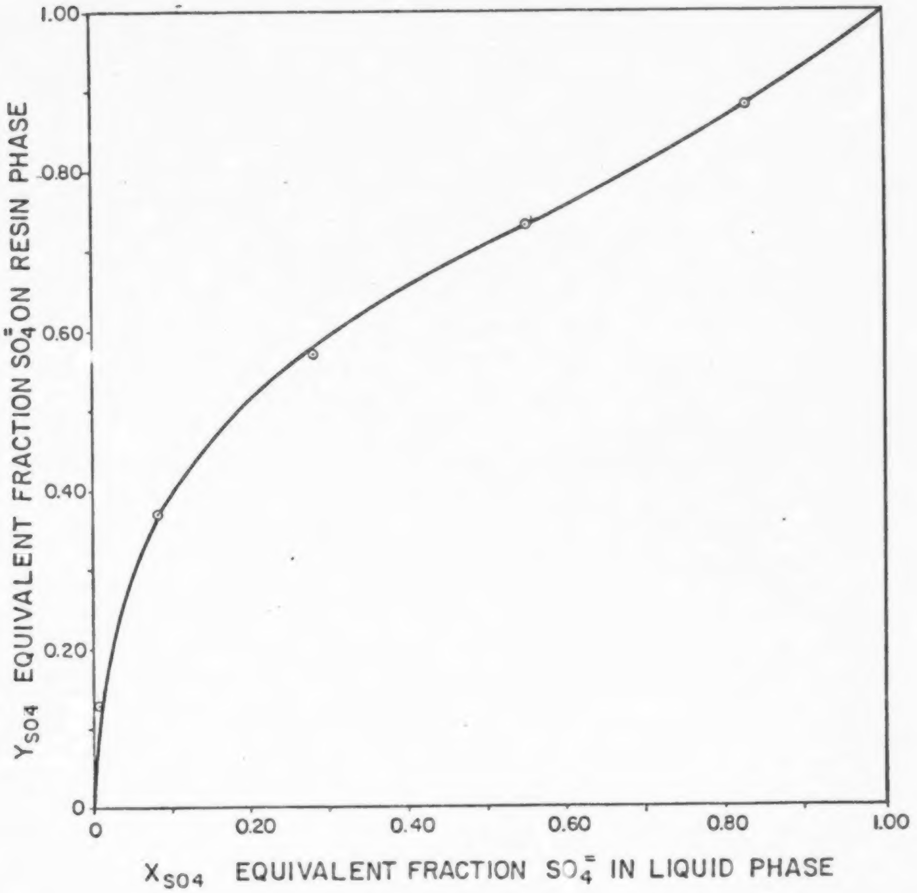
Selectivity Coefficients

Selectivity coefficients can be used to relate column composition to solution composition. These coefficients are used by Anderson (Reference A-3) to relate column composition to solution composition.



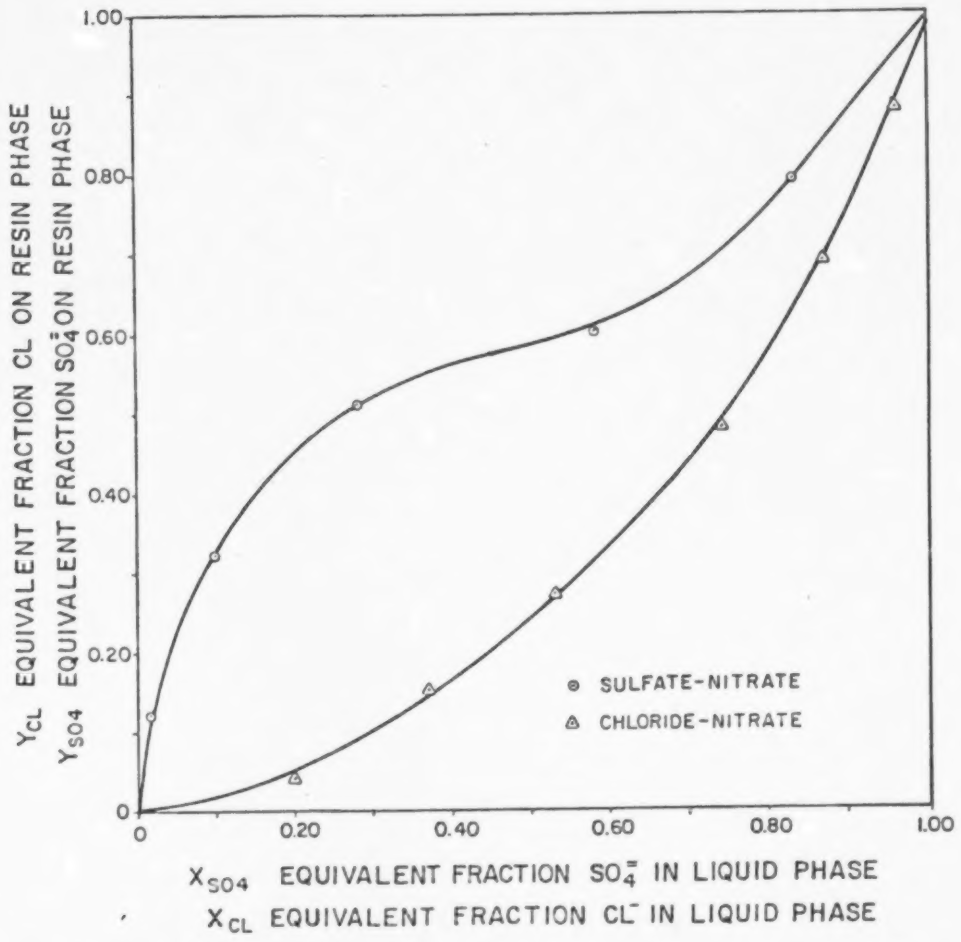
RESIN NUMBER 24
DUOLITE A 101 D, "IMPROVED" POROSITY GEL
STYRENE-DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.3 MEQ/ML

FIGURE A-15 25°C. BINARY ION-EXCHANGE ISOTHERM



RESIN NUMBER 25
DUOLITE A-104, MICROPOROUS GEL
STYRENE-DVB MATRIX
TYPE I & II QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.5 MEQ/ML

FIGURE A-16. 25°C. BINARY ION-EXCHANGE ISOTHERM



RESIN NUMBER 17
AMBERLITE IRA 900, MACROPOROUS RESIN
STYRENE - DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.0 MEQ/ML

FIGURE A-17 25°C. BINARY ION - EXCHANGE ISOTHERM

In the case of two monovalent ions in solution which compete for an ion exchange site on a given resin, the following chemical equilibrium can be written in the case of nitrate and chloride ion competition

$$NO_3^- + \overline{Cl} \rightleftharpoons \overline{NO_3} + Cl^-$$

$$K_{Cl}^{N} = \frac{[\overline{NO_3}]\ [Cl^-]}{[\overline{Cl}]\ \ [NO_3^-]} \qquad \text{Equation (1)}$$

where bracketed terms are concentrations of the ions expressed as equivalents per liter in solution or on the ion exchange resin (barred terms). If Equation (1) is written in terms of equivalent fraction concentration terms, Equation (2) is obtained (see Reference A-3):

$$\frac{\overline{X_N}}{1 - \overline{X_N}} = K_{Cl}^{N} \times \frac{X_N}{1 - X_N} \qquad \text{Equation (2)}$$

where $\overline{X_N}$ = equivalent fraction of nitrate on resin

X_N = equivalent fraction of nitrate in solution

The total concentration of ions in solution and on the resin does not appear in Equation (2).

In the case of a monovalent ion and divalent ion in solution competing for resin ion exchange sites, such as nitrate and sulfate ion competing for sites on an ion exchange resin, the following chemical equilibrium and equilibrium constants can be written:

$$SO_4^= + \overline{2NO_3} \rightleftharpoons 2NO_3^- + \overline{SO_4}$$

$$K_{N}^{S} = \frac{[NO_3^-]^2\ \ [\overline{SO_4}]}{[\overline{NO_3}]^2\ \ [SO_4^=]} \qquad \text{Equation (3)}$$

Again, the unbarred bracketed terms are equivalents per liter of solution, and the barred terms are equivalents of resin bound ions per liter of resin. When Equation (3) is written in terms of equivalent fractions where

$C = [SO_4^=] + [NO_3^-]$ = sum of ion equivalents in solution

$\overline{C} = [\overline{SO_4}] + [\overline{NO_3}]$ = sum of ion equivalents on resin then the equivalent fractions are:

$$X_s = \frac{[SO_4^=]}{C} \; ; \; X_N = \frac{[NO_3^-]}{C}$$

$$\overline{X_s} = \frac{\overline{SO_4}}{\overline{C}} \; ; \; \overline{X_N} = \frac{\overline{NO_3}}{\overline{C}}$$

Substituting in Equation (3)

$$\frac{\overline{X_s}}{(1 - \overline{X_s})^2} = K^s_N \; \frac{\overline{C}}{C} \; \frac{X_s}{(1 - X_s)^2} \qquad \text{Equation (4)}$$

Approximate selectivity coefficients are given in Table A-4 (Reference A-3).

TABLE A-4. APPROXIMATE SELECTIVITY COEFFICIENTS FOR STRONG BASE ANION EXCHANGE RESINS

$K^S_N = 0.04$ $\qquad$ $K^{HCO_3}_{Cl} = 0.5$

$K^N_{Cl} = 4$ $\qquad$ $K^S_{Cl} = 0.15$

$S = SO_4^=$

$N = NO_3^-$ $\qquad$ $HCO_3 = HCO_3^-$

Separation Factors

Clifford and Weber (Reference A-2) have used the separation factor to describe the equilibrium between ions in solution and on the resin. In the case of nitrate and chloride ions

$$\text{Separation factor} = \alpha^N_{Cl} = \frac{[\overline{NO_3}] \; [Cl]}{[\overline{Cl}] \; [NO_3]} = K^N_{Cl} \qquad \text{Equation (5)}$$

in case of monovalent ions α^{N}_{Cl} like K^{N}_{Cl} is independent of concentration.

However, in case of divalent ions

$$\text{Separation factor} = \alpha^{S}_{N} = \frac{[\overline{SO_4}]\ [NO_3^-]}{[\overline{NO_3}]\ [SO_4^=]} \neq K^{S}_{N} \qquad \text{Equation (6)}$$

α^{S}_{N} does not account for concentration effects as K^{S}_{N} does. K^{S}_{N} is, therefore, a more useful parameter when considering groundwaters of different or varying concentration.

Column Effluent Profiles

Multicomponent chromatography theory (References A-4, A-5, A-6, and A-7) can be used to predict the resin phase compositions and concentration profiles of anion exchange resins. The ions removed by the resin become concentrated into enriched zones with a layering according to the resin-ion selectivity coefficients. Figure A-18 shows an idealized chromatographic separation of the four major anions found in groundwater according to the usually observed resin selectivity $SO_4^= > NO_3^- > Cl^- > HCO_3^-$. The sulfate ion being the most preferred ion on the resin is able to displace all other ions (ignoring concentration effects) and thus concentrates at the inlet end of the column. The sulfate ion thus depleted by the inlet or upper portion of the resin is removed from the solution allowing the next preferred ion (nitrate) to concentrate in the next lower band. Chloride and bicarbonate concentrate in the lower portions of the column. As solution continues through the column, the zones grow and move downward with the bicarbonate the first to be eluted from the column followed in order by chloride then nitrate before sulfate breakthrough is achieved.

All anion exchangers studied by Clifford and Weber (Reference A-2) have average sulfate-nitrate separation factors, α^{S}_{N} greater than one. Columns operated at low enough flow rates to allow equilibrium conditions to exist (and low concentrations) would therefore give the chromatographic partitioning shown in Figure A-18. This partitioning may not occur, however, under conditions of high flow rates where column equilibrium is not obtained, at high sulfate to nitrate ratios for some resins, or at high anion concentrations.

The latter concentration effect is often referred to as "electroselectivity" where in dilute solutions the divalent counterions (sulfate) will be preferred by the resin over a monovalent (nitrate) ion. Conversely, at high anion concentration, the monovalent ion may be preferred. As can be seen from Equation (4) when considering a mixture of sulfate and nitrate ions for the equivalent fraction of sulfate on the resin, $\overline{X}_s$, to be greater than the corresponding equivalent fraction in solution, X_s, the total anion concentration, C, must be less than 52 meq/l or approximately 2,500-ppm total anion concentration with a resin where $\overline{C}$ equals 1,300 meq/l.

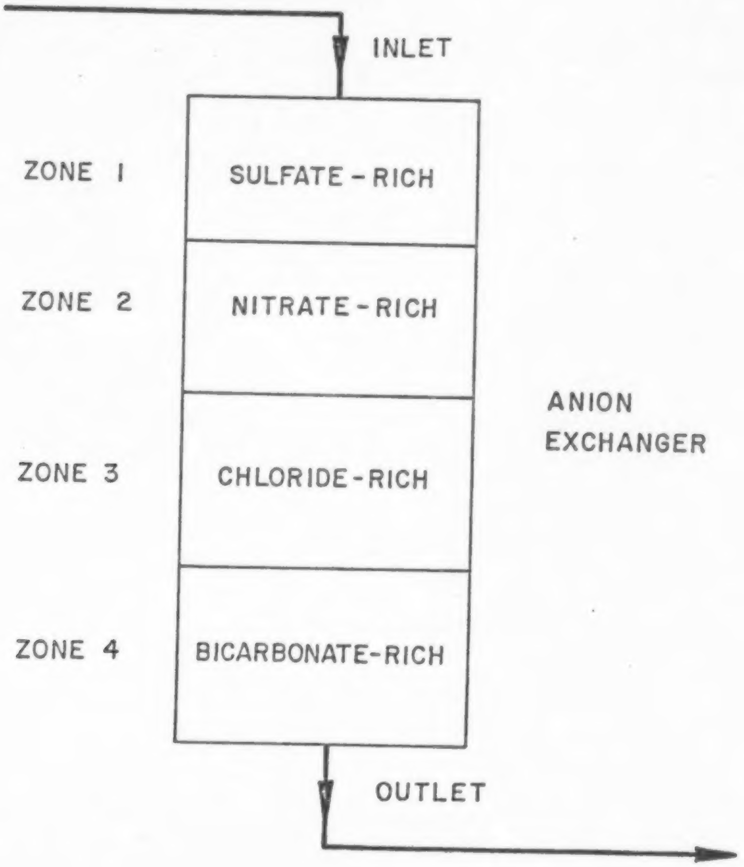

INLET
ZONE 1
SULFATE - RICH
ZONE 2
NITRATE - RICH
ANION
EXCHANGER
ZONE 3
CHLORIDE - RICH
ZONE 4
BICARBONATE-RICH
OUTLET

FIGURE A-18 . CHROMATOGRAPHIC ENRICHMENT OF GROUND WATER ANIONS IN AN EXHAUSTED ANION EXCHANGER

$$\frac{\dfrac{\overline{X}_s}{(1 - \overline{X}_s)^2}}{\dfrac{X_s}{(1 - X_s)^2}} = K^S_N \quad \frac{\overline{C}}{C} > 1 \qquad \text{Equation (7)}$$

$$= K^S_N \quad \overline{C} > C$$

$$K^S_N = 0.04$$

$$\overline{C} = 1{,}300 \text{ meq/l}$$

$$C < 52 \text{ meq/l}$$

At total anion concentrations greater than 52 meq/l, the monovalent nitrate ion would be preferred by the resin and the upper band in Figure A-18 would be enriched with nitrate. Sulfate would thus appear in the column eluate before nitrate ion. Although this high anion concentration will rarely occur in groundwater compositions, electroselectivity favors column regeneration when sulfate ion is to be removed. Thus sulfate is easily removed from spent columns by 1 N sodium chloride in near stoichiometric proportions.

ESTIMATION OF COLUMN PERFORMANCE

From the above resin-ion equilibria relationships, the performance of an ion exchange column for nitrate removal applications can be estimated for flow rates when equilibria can be achieved. Anderson (private communication) has developed a method for approximating the volume of water containing sulfate, nitrate, chloride, and bicarbonate which can be treated by an anion exchange resin before nitrate breakthrough is obtained. Briefly, the method is derived from the following considerations.

As discussed above in groundwaters with anionic concentrations less than 2,500 ppm, strong base anion resins show the following relative selectivities:

$$SO_4^{=} > NO_3^{-} > Cl^{-} > HCO_3^{-}$$

The column will become partitioned in zones as shown in Figure A-18. As the column is eluted with a continuing flow of feed water, Zone 1 and Zone 2 will grow and expand downward until nitrate breakthrough begins to occur. Zone 1 will have a composition in equilibrium with the feed water and will contain sulfate and nitrate. Zone 2 will be in equilibrium with the water leaving Zone 1 and will contain nitrate with no sulfate. From simultaneous equations expressing sulfate and nitrate balances, the amount of nitrate on the column at the end of the run can be estimated as follows:

f = fraction of bed in Zone 1
$BV(N)$ = bed volume of effluent to nitrate breakthrough
$\overline{C}$ = capacity of resin in eq/l
a = sulfate concentration in feed meq/l
b = nitrate concentration in feed meq/l

The sulfate balances after passage of BV(N) through the column is

$$\overline{X_s}\ \overline{C}\ f = (a \times 10^{-3})\ BV(N) \qquad \text{Equation (8)}$$

The nitrate balance is

$$[(1 - \overline{X_s})\ (\overline{X'_N})\ \overline{Cf}] + [\overline{X'_N}\ \overline{C}\ (1 - f)] = (b \times 10^{-3})\ \ BV(N) \qquad \text{Equation (9)}$$

Where $\overline{X'_N}$ is the fraction of the nonsulfate portion of the resin in the nitrate form in both zones. The first bracketed term represents the equivalents of nitrate in Zone 1 of the column, and the second bracketed term represents the nitrate equivalents in Zone 2. Solving the two above equations simultaneously, the following is obtained:

$$BV(N) = \frac{\overline{X'_N}\ \ \overline{C}}{a\ \overline{X'_N} + b} \qquad \text{Equation (10)}$$

$\overline{X'_N}$ represents the fraction of Zone 2 in the nitrate form as well as the fraction of the nonsulfate portion of Zone 1. The two zones will be initially established as thin sections at the top of the column. As Zone 1 grows, nitrate ion of Zone 2 is displaced and moves down the column to enrich Zone 2 in more nitrate. The nitrate concentration in equilibrium with the enriched nitrate Zone 2 will be greater than b but less than b + a.

The nitrate concentration in Zone 2, X'_N, is estimated as (b + 0.8.a). The fraction of the nonsulfate portion of the column in the nitrate form will be $\overline{X'_N}$ which is related to X'_N in Equation (11).

$$n = \frac{\overline{X'_N}}{1 - \overline{X'_N}} = K^{N}_{Cl}\ \ \frac{\frac{b + .8a}{C}}{1 - \frac{b + .8a}{C}} \qquad \text{Equation (11)}$$

then:

$$\overline{X'_N} = \frac{n}{1 + n} \qquad \text{Equation (12)}$$

by substituting Equation (12) into Equation (10), the following is obtained:

$$BV(N) = \frac{\bar{C}}{a + b + b/n} \times 10^3 \qquad \text{Equation (13)}$$

As an example, BV(N) can be calculated from Equations (12) and (13) for Run 11078. Bicarbonate and chloride concentrations are considered as chloride

$a = 5.93$ meq/l

$b = 1.56$ meq/l

$c = 4.15$ meq/l

$K^N_{Cl} = 4$

$\overline{C} = 1.3$ eq/l

$C = 11.64$ meq/l

$$n = 4 \times \frac{\frac{1.56 + .8 \times 5.93}{11.64}}{1 - \frac{1.56 + .8 \times 5.93}{11.64}} = 4.69$$

$$BV(N) = \frac{\overline{C}}{a + b + b/n} \times 10^3 = \frac{1.3 \times 10^3}{5.93 + 1.56 \div \frac{1.56}{4.69}} = 166$$

The observed experimental value for BV(N) is 157 in good agreement with the estimated value. The observed and estimated values for the column runs are discussed in the following section.

Equation (13) was used to estimate bed volumes to nitrate breakthrough for a number of water compositions. The estimates are given in Table A-5.

TABLE A-5. ESTIMATES OF COLUMN CAPACITY (C = 1.4 eq/l)

		BV(N		
NO_3^-	$SO_4^=$	$(Cl^- + HCO_3^-) = 1$	$(Cl^- + HCO_3^-) = 2$	$(Cl^- + HCO_3^-) = 3$
1	.5	825	747	682
1	1	646	607	573
1	2	447	433	421
1	3	340	334	328
1	4	274	271	268
1	5	230	228	226
1.3	.5	696	636	585
1.3	1	563	530	501
1.3	2	405	392	380
1.3	3	315	309	303
1.3	4	258	254	251
1.3	5	218	216	214
1.6	.5	603	556	515
1.6	1	500	472	447
1.6	2	370	359	348
1.6	3	294	288	282
1.6	4	243	240	237
1.6	5	208	205	203

*Concentrations in meq/l

The chloride and bicarbonate are combined because of the similarity in the resin selectivity for these two ions. The estimates are also based on a use of a fully regenerated resin with a capacity of 1.4 eq/l. To determine the capacity of a column loaded with a resin with a capacity of 1.0 eq/l, the BV(N) values in the table must be multiplied by 1.0/1.4. If the resin having an anion exchange capacity of 1.4 eq/l is not fully regenerated, i.e., the equivalent fraction of resin in the nitrate form $X_N \neq O$, the BV(N) values listed in Table A-5 must be multiplied by $(1 - X_N)$ to obtain the nitrate capacity, BV(N) of a column.

NITRATE LEAKAGE FROM INCOMPLETELY REGENERATED COLUMNS

Because it may not be practical to use fully regenerated resin columns for nitrate removal, nitrate ion will appear in the effluent from the column before the breakthrough point is obtained. The concentration of nitrate leakage from a column will depend on the total anion (chloride) concentration and the equivalent fraction of the resin in the nitrate form, X_N, at the exit end of the column. Equation (2) can be used to estimate, X_N, the equivalent fraction of nitrate in the effluent. As an example, Table A-6 gives values of nitrate leakage derived from Equation (2) for columns of various values of X_N with a water having a total anion concentration of 10.0 meq/l entering the column.

TABLE A-6. ESTIMATE OF NITRATE LEAKAGE THROUGH INCOMPLETELY REGENERATED COLUMNS

		Nitrate Leakage	
$\overline{X_N}$	X_N	NO_3^- meq/l	NO_3^- ppm
.1	.027	.27	16.7
.2	.059	.59	36.5
.3	.097	.97	60.0
.4	.143	1.43	88.7
.5	.200	2.00	124
.6	.273	2.73	169
.7	.368	3.68	228
.8	.500	5.00	310
.9	.692	6.92	429

C = Total anion concentration = 10 meq/l

$K_C^N = 4$

$\overline{X_N}$ = Fraction of resin in nitrate form after regeneration

DISCUSSION OF RESULTS OF TWO-INCH COLUMN TESTS

Breakthrough Curves

Several tests were made using 2-inch-diameter columns with a 24-inch bed depth of resin. The test procedures are described in Section 2 of this report. The tests were conducted with Well 3 water as well as synthetic blends to determine column capacity with these waters and verify the above estimates of column capacity. Table A-3 lists the results and conditions for these tests.

Inspection of the breakthrough curves shows the formation of sulfate enriched zones only under certain conditions. Run 02199 (Figure A-6) and Run 02219 (Figure A-5) were both run with the same feed water composition; however, Figure A-5 shows nitrate breakthrough occurring well before sulfate breakthrough along with a nitrate peak above the influent concentration. This breakthrough pattern is to be expected when a sulfate enriched zone is formed at the top of the column and a nitrate enriched zone is formed at the bottom as discussed in the above section. As the sulfate enriched zone grows after nitrate breakthrough, sulfate ion displaces the resin-bound nitrate in the nitrate zone. The nitrate effluent concentration will exceed the influent concentration because of this displacement by sulfate. A different effluent profile is obtained with the Type II resin, A-104, in Run 02199 which shows a nearly simultaneous breakthrough for nitrate and sulfate ions indicating that the enriched sulfate and nitrate zones do not occur at these concentrations. This indicates the selectivity under these conditions for Type I resin is $SO_4 > NO_3$ and for Type II resin is $SO_4^{=} = NO_3^-$. In Run 03059 (Figure

A-7) with the Type II resin, sulfate ion breakthrough occurs before nitrate. Run 03299 (Figure A-8) shows the same behavior as A-104 resin. Resins A-101D, A-104, and Dowex SAR are of the microporous type. When the macroporous resins are compared, nitrate and sulfate breakthrough occurred nearly simultaneously without nitrate effluent concentration exceeding the influent concentration for both Type I and Type II resins (Runs 06229 and 06279, Figures A-9 and A-10). Thus indicating that chromatographic partitioning does not occur with the macroporous resins at these concentrations.

Run 02290 (Figure A-11) with A-101D resin showed nitrate breakthrough prior to sulfate, but the rise of effluent nitrate concentrations above influent concentration is not as apparent as in Run 02219. Run 03050 (Figure A-19) shows the typical breakthrough pattern of the A-101D resin, however, Run 03140 (Figure A-20) does not which can be attributed to nonequilibrium at high flow rates.

The conditions under which chromatographic partitioning did or did not appear as indicated by column effluent profiles are compared in Table A-7. Only one resin, A-101D, has thus far exhibited an effluent pattern suggestive of chromatographic separation. At flow rates above 0.33 BV per minute (Runs 02260, 02230, and 03140), the chromatographic pattern either does not occur or is distorted by high flow rates. These results can be correlated with the isotherm data obtained by Clifford (Reference A-2).

TABLE A-7. COMPARISON OF COLUMN EXPERIMENTS

Run No.	Effluent Pattern Suggestive of Chromatographic Partitioning	Resin (Type)	Resin Porosity*	meq $SO_4^=$	meq NO_3^-	$\frac{\text{meq } SO_4^=}{\text{meq } NO_3^-}$	Flow Rate BV/min
11078	--	A-101D(I)	micro	5.93	1.56	3.81	.33
02199	no	A104(II)	micro	4.69	1.11	4.23	.33
02219	yes	A-101D(I)	micro	4.69	1.11	4.23	.33
03059	no	A104(II)	micro	6.70	1.92	3.49	.33
03299	no	A104(II)	micro	7.65	1.74	4.40	.33
06229	no	IRA-900(I)	macro	7.18	1.80	3.99	.33
06279	no	IRA-910(II)	macro	7.18	1.80	3.99	.33
02290	yes	A-101D(I)	micro	7.33	1.71	4.29	.36
02260	no	A-101D(I)	micro	7.75	1.26	6.15	1.10
02230	no	A-101D(I)	micro	6.87	1.49	4.61	1.56
03050	yes	A-101D(I)	micro	3.64	1.63	2.23	.33
03140	no	A-101D(I)	micro	8.33	1.12	7.43	1.00
03069	yes	A-101D(I)	micro	3.35	0.85	3.94	.33

---

*Duolite 101D has a moisture content of 48 to 55 percent; Duolite A104 has moisture content of 40 to 46 percent; Dowex SAR moisture content equals 38 to 45 percent; IRA-900 has a moisture content of 60 to 64 percent; and IRA-910 has a moisture content of 50 to 55 percent.

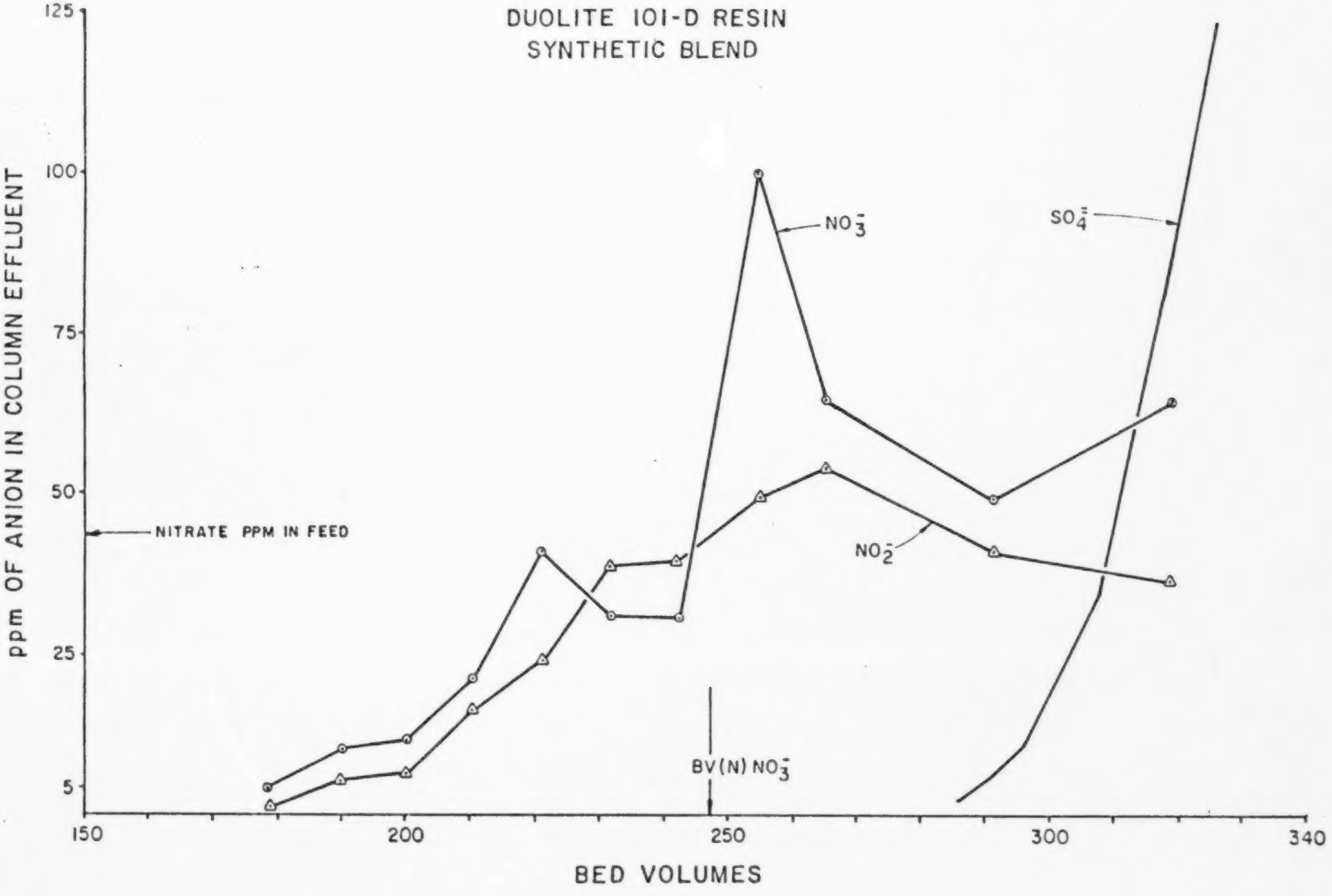


FIGURE A-19 . ION EXCHANGE COLUMN EXPERIMENT 03050

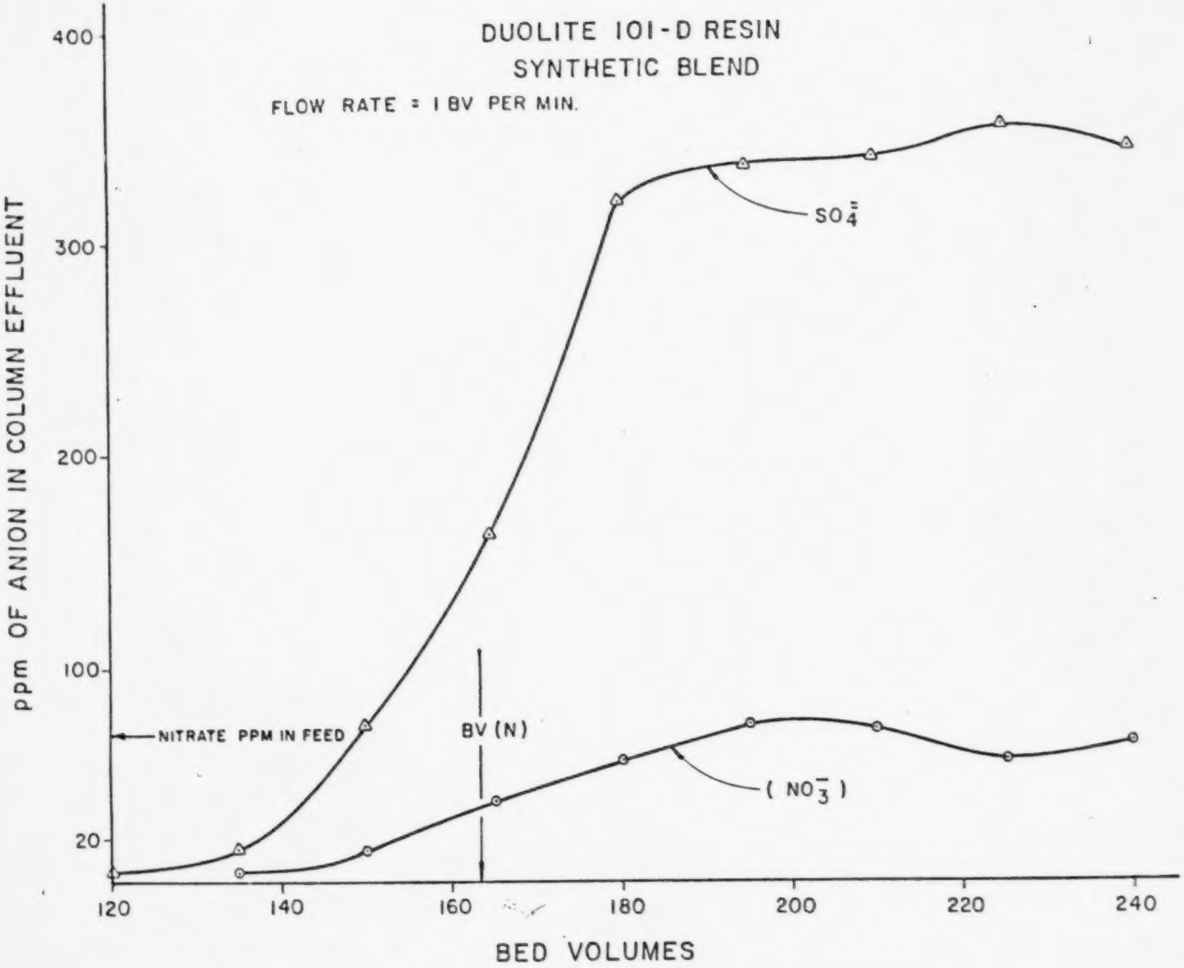
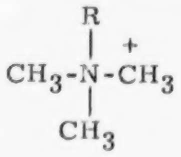


FIGURE A-20 . ION EXCHANGE COLUMN EXPERIMENT 03140

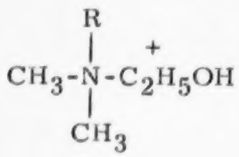
Figures A-15, A-16, and A-17 show isotherms for three of the resins tested. For the IRA-900 resin, an S-shaped isotherm is quite obvious indicating that at high sulfate equivalent fractions, the resin becomes more selective for nitrate than sulfate. Similar but less pronounced S shape of the isotherm for A-104 resin is also shown, Figure A-16. Thus it is reasonable that these two resins would not show the effluent pattern suggestive of chromatograpic partitioning at these high sulfate concentrations but show diminished or equal sulfate over nitrate selectivity. The isotherm for A-101D, Figure A-15, does not show the S-shaped isotherm, therefore, the resin is able to retain the sulfate over nitrate selectivity at the high sulfate concentrations.

These limited results indicate that the differences between A-104 and A-101D may be significant in considering sulfate to nitrate selectivity. The difference between the two resins is one of moisture content, degree of cross linking and the type of pendant groups on the quaternary nitrogen as shown below:



$$CH_3\text{-}\overset{\overset{R}{|}}{\underset{\underset{CH_3}{|}}{N^{+}}}\text{-}CH_3$$

Type I
A-101D



$$CH_3\text{-}\overset{\overset{R}{|}}{\underset{\underset{CH_3}{|}}{N^{+}}}\text{-}C_2H_5OH$$

Type II
A-104

Resins having varied pendant groups are being synthesized and will be column tested for nitrate selectivity. Previous work (Reference A-2) has indicated that the kind of substituents on the functional amine group is one of several factors which can influence the nitrate to sulfate selectivity. For example, the higher the amine (secondary, tertiary, or quaternary), the less selectivity for sulfate over nitrate. No apparent effect was noted on nitrate to chloride selectivity for those amines. However, it is not possible to predict either how or to what extent specific structural changes about the quaternary nitrogen will influence nitrate selectivity.

Column Capacity

The column capacity for nitrate removal can be estimated from the composition of the feed water and compared to the experimentally obtained values. Bed volumes to nitrate breakthrough BV(N) were estimated from Equation (13) and compared to the experimentally obtained values. These are compared in Table A-8.

TABLE A-8. ESTIMATION OF COLUMN CAPACITY USING EQUATION (13)

Run No.	BV(N) Experimental	BV(N) Estimated Equation (13)	Percent Deviation $\frac{\text{Estimate-Experimental}}{\text{Estimate}} \times 100$
11078	157	166	+5.42
02199	240	229	-4.80
02219	198	210	+5.71
03059	172	154	-11.69
03299	184	143	-28.67
06229	140	106	-32.07
06279	122	106	-15.09
02290	147	149	+1.34
02260*	159	140	-13.57
02230*	176	150	-17.33
03069	300	289	-3.81
03050	248	234	-5.98
03140*	163	135	-20.74

*Runs made at high flow velocity.

Equation (13) gives the best estimates for the A-101D resin if results of runs made at high flow velocity are ignored because of the nonequilibrium conditions. For this resin, the average deviation of the experimental value from the estimated value is ±4.45 percent. The A-104, Dowex SAR, IRA-900, and IRA-910 all give higher experimental values than the estimated value. Equation (13) was derived for those cases where chromatographic partitioning of sulfate and nitrate occur on the resin column. It is therefore a good estimate for those cases but can be as much as 30 percent too low for the other resins which were studied. It is interesting to note that at high flow velocities with the A-101D resin, Equation (13) can give estimates 20 percent too low. This must be attributed to kinetic effects in the complex reacting system.

Columns where partitioning of sulfate and nitrate do not occur but form a zone homogeneous in nitrate and sulfate can be estimated using different relationships. Assuming that nitrate and sulfate ions are absorbed on the resin in preference to chloride and bicarbonate, an estimation of column capacity can be made by considering these ions alone:

$$BV(N) = \frac{\overline{C}}{\text{meq } SO_4^{=} + \text{meq } NO_3^{-}} \qquad \text{Equation (14)}$$

Estimates based on Equation (14) are given in Table A-9. Again, if runs at high flow rates are discounted, the average deviation for all other runs is ±7.2 percent.

TABLE A-9. ESTIMATION OF COLUMN CAPACITY USING EQUATION (14)

Run No.	BV(N) Experimental	BV(N) Estimated Equation (14)	Percent Deviation $\frac{\text{Estimate-Experimental}}{\text{Estimate}} \times 100$
11078	157	173	+9.2
02199	240	241	+0.4
02219	198	221	+10.4
03059	172	162	-6.2
03299	184	149	-23.5
06229	140	123	-13.8
06279	122	123	+0.8
02290	147	153	+3.9
02260*	159	144	-10.4
02230*	176	156	-12.8
03069	300	309	2.9
03050	248	246	-0.8
03140*	163	138	-18.1

*Runs made at high flow rates.

It should be pointed out that the water compositions thus far investigated in this work are high in sulfate content. Use of Equation (13) should apply to waters of low sulfate concentration because it includes the effect of chloride and bicarbonate ions. Equation (14) does not and will not apply to solutions
and bicarbonate ions. Equation (14) does not and will not apply to solutions
of low sulfate where chloride and nitrate are present. Data from Clifford and Weber (Reference A-2) for Ionac AFP-100 (a Type I resin) is as follows:

Resin Capacity meq/l = 1.07

HCO_3^- = 1.0 meq/l

Cl^- = 1.5

NO_3^- = 1.5

$SO_4^=$ = 1.5

BV(N) = 295 experimental

BV(N) = 316 Equation (13); % deviation = 6.6

BV(N) = 357 Equation (14); % deviation = 17.4

SECTION 5

RESULTS OF ION EXCHANGE PILOT COLUMN TESTS

INITIAL TEST RUNS - MODE A OPERATION

The installation of the HI-FLO 5 System was previously described. Operation of the system was initiated on May 31, 1979, without any further modification using Well 3 water of the following composition:

NO_3^- meq/l	= 1.80
HCO_3^-	= 2.50
Cl	= 2.82
$SO_4^=$	= 7.18

Bed capacity is estimated as

BV(N) = 139 Equation (13)

BV(N) = 145 Equation (14)

Initial test conditions are referred to as Mode A operation and were as follows:

Mode A

Program Sequence

Service	- 11.74 gpm to breakthrough.
Backwash	- 10 gpm for 10 minutes.
Brine Rinse	- Variable from 20 to 40 minutes. Determined by quantity of water put into brine tank.
Slow Rinse	- 55 minutes minus brine rinse time.
Conditioning Rinse	- 10 gpm for 10 minutes.

Other Conditions

Brine Concentration - Approximately 12 percent.
Brine and flow distributor provided by vendor.

The breakthrough curve for virgin resin exhaustion gave BV(N) = 125 BV of treated water. Some nitrate leakage was detected during exhaustion on the first and subsequent runs indicating hydraulic leakage or channeling. Salt dosage was varied by lengthening the brine tank refill time and/or adding extra water to the brine tank.

In this particular mode, the system was operated to exhaust the resin and regenerate on alternate days. Data obtained from the first series of runs are given in Table A-10. Salt dosages listed in Table A-10 show no effect on bed capacity or nitrate level in product water. Performance indicated that treatment of 123 BV (4,011 gallons) would require about 121 pounds of salt (27.8 pounds salt per cubic foot of resin).

TABLE A-10. ANION EXCHANGE PILOT COLUMN DATA

Run No.	Estimate of Salt Dosage (lb/cu ft)	Bed Volumes To NO_3^- Break	Highest ppm NO_3^- in Product
05319	Virgin	125	8.8
06059	27.7	108	--
06079	27.7	123	19
06139	36.9	124	15
06189	36.9	127	18
06209	36.9	127	13
06229	33.4	117	20
06269	33.4	127	9
07019	33.4	132	25

Operation of the pilot column was continued in Mode A to generate data in Figure A-21 which shows nitrate leakage at various levels of salt dosages used for regeneration. Because of the high salt dosage requirements, the mechanical and hydraulic design of the pilot column was closely examined to seek more efficient operation.

MODIFICATION OF PILOT COLUMN AND MODE B OPERATION

As received from the vendor, the HI-FLO 5 had a 1-1/2-inch inlet pipe at the top of the ion exchange tank as shown in Figure A-22 (a). This was modified as shown in Figure A-22 (b) using 1-inch PVC fittings and pipes to give a four-point flow distribution at the top of the column. It is believed that at the low flow rates of the dense brine (12 percent), the configuration in Figure A-22 (a) promoted channeling around the resin bed by allowing the denser solution to rapidly flow to the bottom of the bed.

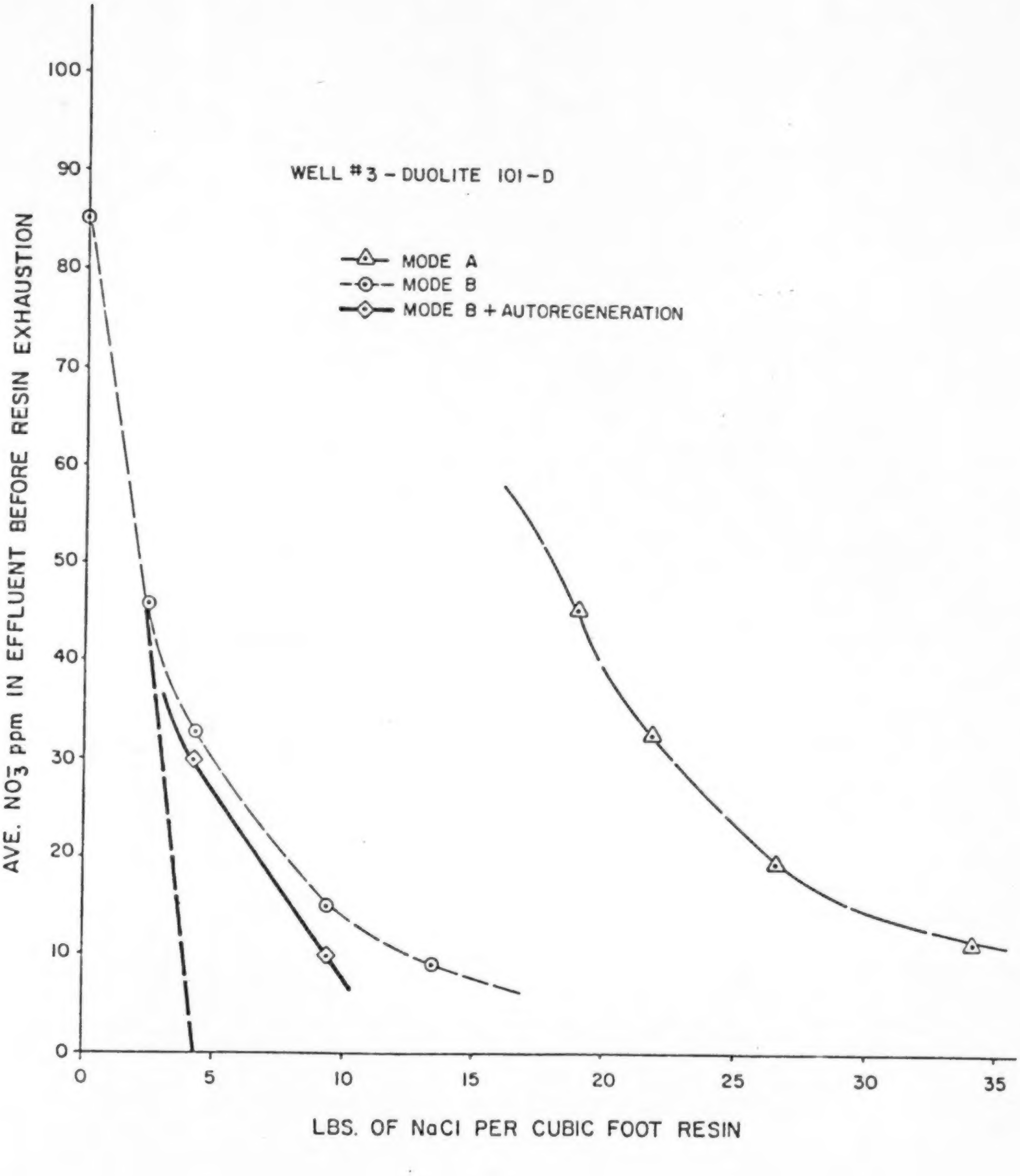
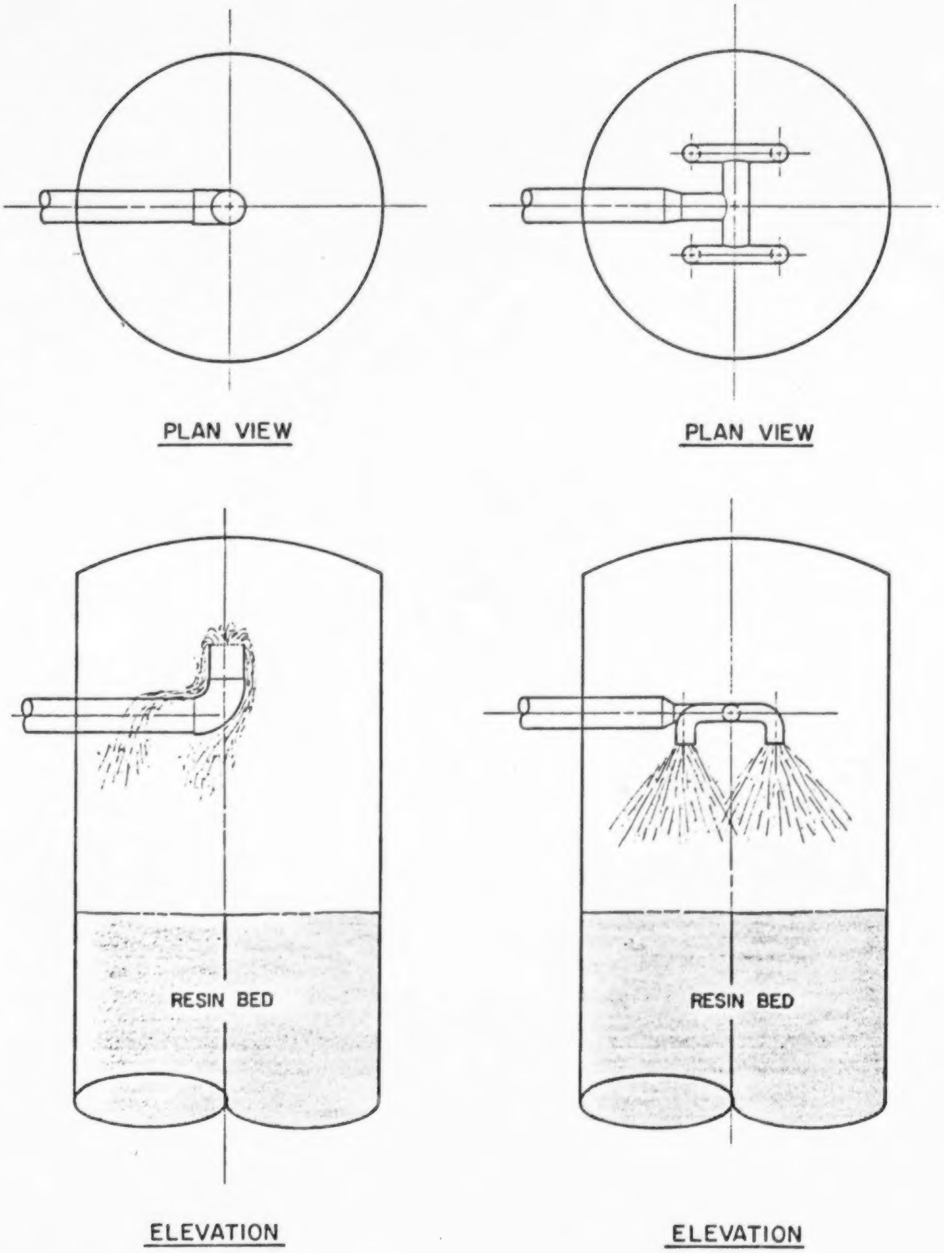


FIGURE A-21. PILOT COLUMN ION EXCHANGE SYSTEM NITRATE LEAKAGE DEPENDENCE ON MODE OF OPERATION AND SALT LOADING


PLAN VIEW
PLAN VIEW
RESIN BED
RESIN BED
ELEVATION
ELEVATION

(a) (b)

FIGURE A-22. FLOW DISTRIBUTION IN VENDOR SUPPLIED SYSTEM (a) AND MODIFIED SYSTEM (b)

The operation was also modified to give a less dense brine (ca 3 to 6 percent) and declassify (evenly distribute) the bed after regeneration. As previously discussed, the A-101D resin forms an enriched sulfate zone at the top of the column and a nitrate rich zone at the bottom of the column.

This separation is suited for downflow regeneration since the nitrate is already at the exit end of the column thus obviating the necessity to move nitrate from top to bottom (as would be required by upflow regeneration). Incomplete regeneration would then leave a nitrate rich resin zone at the exit of the column from which high nitrate leakage could occur. The program sequence was thus changed to regenerate before backwashing. Backwashing was also done intermittently to aid in declassifying the enriched zones of the bed.

The operation was also modified to give the slowest rate of brine draw which could be achieved with this system. Brine draw rate was reduced to give 3 to 6 percent salt content after mixing with eductor water. To accomplish this, a manually operated shutoff valve was installed in the brine line to control the amount of time that the brine could be drawn into the eductor. This provided a positive control over brine flow into the system. Salt dosage per run could be measured by the fall in brine level in the brine tank and measurement of salt content of the brine. Since this brine draw rate proved to be quite constant, timing the period of brine draw was also used to control the salt dosage.

Mode B operation of the pilot column was set as follows:

Mode B

Program Sequence

Service - 12 to 45 gpm to breakthrough.

Brine Rinse - Variable by manually opening and closing valve in brine line; varied in pilot plant from 7.5 to 45 minutes at 5 BV per hour.

Slow Rinse - 45 minutes at 3 gpm.

Conditioning Rinse - 10 gpm for 10 minutes (intermittent to declassify resin).

Other Conditions

Brine Concentration - 3 to 6 percent.

Brine flow distributor redesigned as described in text (Figure A-22 [b]).

A comparison of the performances of the two different modes of operation is given in Figure A-23. Nearly equivalent performances are obtained operating in Mode A with 22 pounds of regenerant per cubic foot of resin and Mode B with 4.5 pounds of regenerant per cubic foot of resin. This represents an 80 percent reduction in salt requirements. Increasing the salt loading to 13.5 pounds and operation in Mode B gives slightly longer bed life and a much lower nitrate leakage.

In these cases, the bed does not become completely regenerated as is indicated by the nitrate leakages and the shorter bed lives as compared to laboratory column experiments reported above.

A further comparison of several pilot column runs using the two modes of operation is shown in Figure A-21. In Mode A operation, salt load requirements are consistently higher for equivalent nitrate leakages found for Mode B. For very low salt loadings on the Mode B curve, a rapid drop in nitrate leakage is shown for small increases in salt loading. Extrapolation of the slope (heavy dashed line) intercepts at a salt loading of 4.7 which corresponds to one equivalent of resin being regenerated by one equivalent of salt. This indicates that sulfate is being removed stoichiometrically and occurs in the early portion of the regeneration period. The curved portion of the Mode B curve represents nitrate removal. In two runs of Mode B operation, the system was allowed to operate past the breakthrough point and allow the resin to "autoregenerate" or allow sulfate to accumulate and throw off excess nitrate. (This also simulates partial regeneration by an R.O. brine.)

It is seen that salt savings can be realized when regenerating the nitrate portion of the bed after "autoregeneration." For example, to operate the system to give a nitrate leakage of 7.5 ppm, the salt loadings would be:

Mode	Salt Loading (lb/cu ft)
A	Over 35
B	15
B+ autoregeneration	9.5

This data indicates that regeneration by an R.O. brine from Well 3 offers a potential savings of 37 percent in salt requirements at this level of nitrate leakage.

This suggests that the main plant for nitrate removal would be an ion exchange system. Addition of an R.O. system would be useful for brine generation to reduce regenerant salt requirements. A bonus would be blending of R.O. product back into the process stream to reduce sulfate and TDS loads on the resin as well as providing a lower TDS in product water.

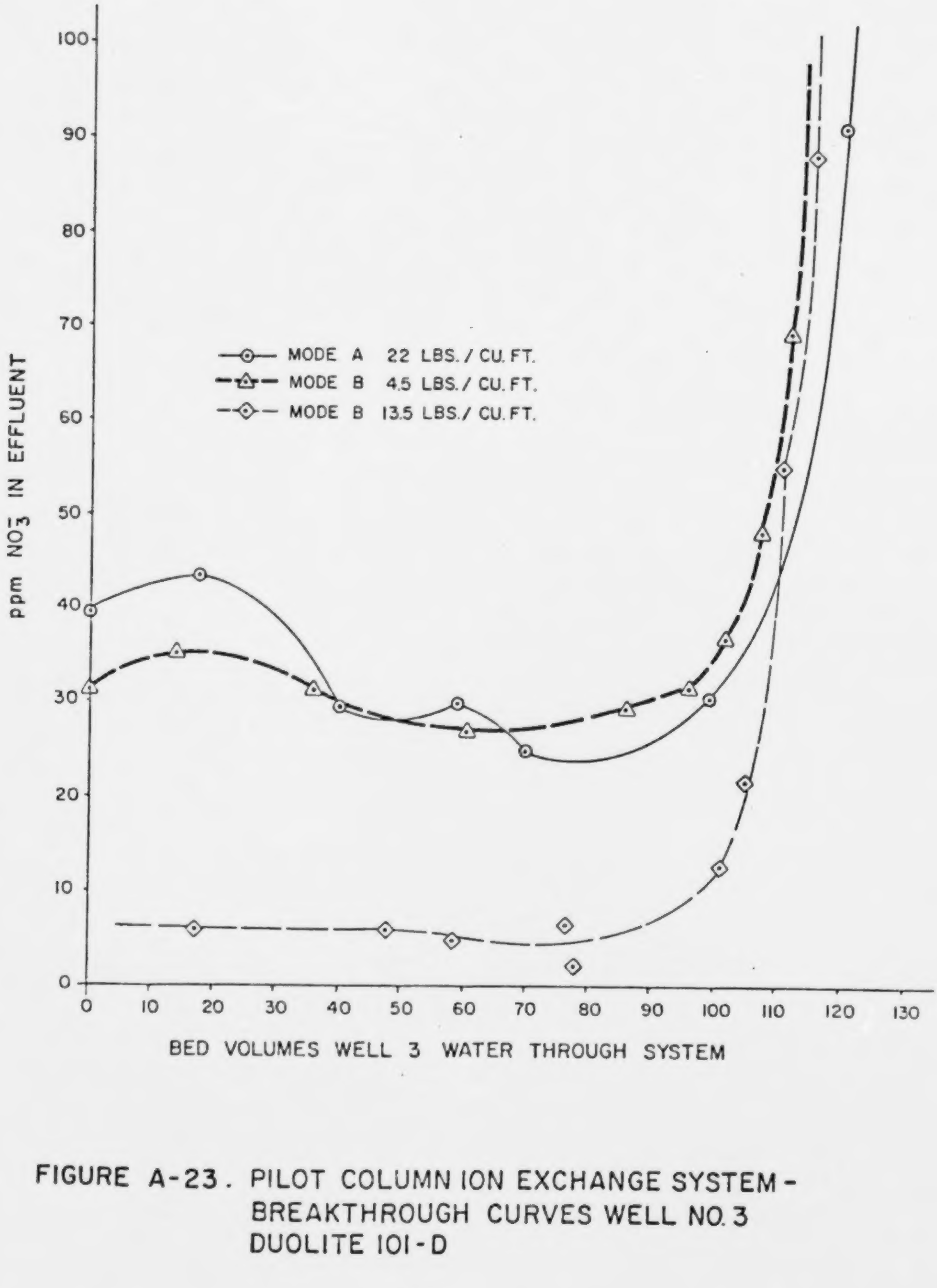


FIGURE A-23. PILOT COLUMN ION EXCHANGE SYSTEM - BREAKTHROUGH CURVES WELL NO. 3 DUOLITE 101-D

WASTE BRINE COMPOSITION

Samples of waste brine were analyzed for nitrate and sulfate during Mode B regeneration runs with the pilot column. The resin was rinsed with 6 percent brine for a period of 82 minutes to promote complete nitrate removal. Sulfate and nitrate concentrations are plotted in Figure A-24 versus BV of waste brine leaving the system. No samples were taken until 1 BV had been discharged from the system. The first BV of brine into the system becomes diluted with the water above the resin bed. Full-strength brine was not obtained until the second BV was discharged. However, it can be seen that the first BV discharged was very high in sulfate ion. It appears again that sulfate is efficiently removed by the brine (approximately 1.5 BV). The regeneration capacity of the brine in the first BV is consumed by sulfate removal and is not effective in removing nitrate.

Planimeter measurements of area under the nitrate curve give the following nitrate removals per BV:

Bed Volume of Brine Discharged From System	% Nitrate Removed by Each Bed Volume	Cumulative Percentage of Nitrate Removed
1st	3.26	3.26
2nd	30.44	33.70
3rd	38.04	71.74
4th	19.13	90.87
5th	6.96	97.83
6th	2.17	100.00

Also from integration of the nitrate curve, it is estimated that 36.6 equivalents of nitrate were removed in 6 BV. This represents 23 percent of the resin bed capacity.

FLOW RATE STUDIES

It is economically advantageous to operate ion exchange columns at high flow rates to reduce the cost of capital equipment and resin quantity.

A series of short-term exploratory runs were made to determine the effect of flow rate during the service cycle. The system was operated in regeneration Mode B as described above. The data for these runs are given in Table A-11. Flow rates were varied from approximately 4 to 10 gpm per square foot. Each time, the resin was regenerated in regeneration Mode B with 4.48 pounds of sodium chloride per cubic foot of resin. This level of regeneration was chosen because it is believed that the resin is more sensitive to flow rate in a state of partial regeneration. Data suggested that the lowest nitrate leakage was obtained with the highest flow rate which was not expected.

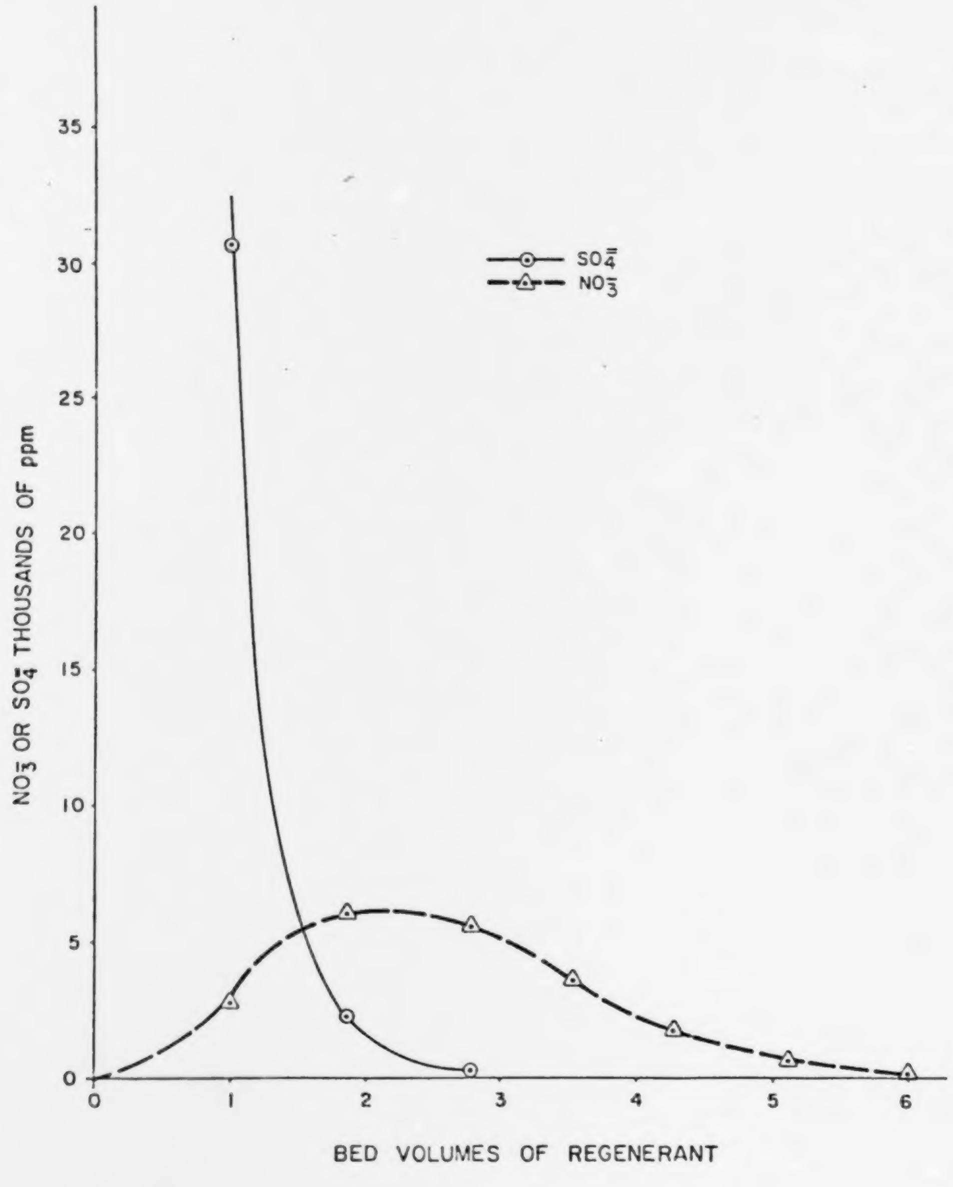


FIGURE A-24. SULFATE AND NITRATE IN 6% BRINE DISCHARGE FROM SYSTEM

TABLE A-11. ION EXCHANGE PILOT COLUMN EFFECT OF SERVICE FLOW RATE ON NITRATE LEAKAGE [a,b]

Flow Rate (BV/hr)	Flow Rate (gpm/sq ft)	Average Nitrate Leakage (ppm)
39.7	9.9	38.1
32.0	8.0	47.6
18.4	4.6	41.6
16.8	4.2	42.4
16.4	4.1	42.8
20.3	5.1	43.5
20.4	5.1	40.6
20.6	5.1	40.0
23.6	5.9	46.1
23.6	5.9	45.5
25.8	6.4	48.8

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[a] Regeneration Mode B with 4.48 lb/cu ft resin.
[b] Well 3 nitrate = 87 ppm.

A longer series of tests was then made to further investigate the effects of higher flow rates. Two-inch IPS pipe was installed as the inlet and outlet to the HI-FLO 5 to allow flow rates higher than 10 gpm. A 1-inch water meter was also installed.

The results of 31 tests given in Table A-12 show no loss of column efficiency at the highest obtainable flow rate of 1.38 BV per minute (6.02 gallons per cubic foot of resin or 22.5 gpm per square foot of resin). Breakthrough curves for representative runs are shown in Figures A-25 through A-28.

COMPARISON OF PILOT COLUMN TESTS WITH ESTIMATES OF PERFORMANCE

Method

The regenerant requirements for any given nitrate leakage through a column of resin and for treatment of unit quantity of water can be estimated in the following steps:

Step 1 - Estimate maximum column capacity.
Step 2 - Estimate residual nitrate on exhausted resin.
Step 3 - Estimate quantity of water treated to nitrate breakthrough at given nitrate leakage.
Step 4 - Estimate regenerant requirements.

This method is illustrated below using McFarland Well 3 water and A-101D resin. Although the method is applicable for other water compositions and other strong base anion exchange resins, only pilot column data has been obtained for Well 3 compositions and the particular resin used.

Maximum Column Capacity - Step 1

Estimates of maximum column capacity for completely regenerated columns can be made using Equation (13) or Equation (14) for McFarland Well 3 of the following composition with resin having an exchange capacity of 1.3 eq/l:

NO_3^-	= 97.5 ppm	= 1.57 meq/l
HCO_3^-	= 82.5	= 1.35
Cl	= 95.9	= 2.70
$SO_4^=$	= 325	= 6.77
Total Anion		12.39

BV(N) from Equation (13) = 150

BV(N) from Equation (14) = 156

TABLE A-12. PILOT COLUMN DATA

Run No.	BV/Min	Regenerant (lb NaCl/ft^3)	Average NO$_3^-$ Leakage (ppm)	BV(N)	Figure No.
01220	0.63	2.29	40	72	
01220A	0.63	2.58	38	72	
01240	0.63	2.29	40	81	
01280	0.34	2.29	50		
01280A	0.34	2.29	37	64	
01300	0.34	2.29	45		
01300A	0.34	2.58	37	53	
02060	0.34	2.29	43	42	
02080	0.34	2.29	45	80	28
02120	0.34	2.00	48		
02180	0.23	2.29	44	75	
02210	1.15	2.15	45	65	
02220	1.38	1.72	55		
02220A	1.25	2.87	43	75	28
02250	1.38	2.29	44	75	
02260	1.38	4.86	30		
02270	1.38	4.86	29	108	27
02280	1.38	5.72	25	108	
02290	0.34	4.86	27	90	
02300	0.34	4.86	25	92	
03020	0.23	5.44	28	114	27
03030	0.23	5.72	28	113	
03070	0.69	4.58	30	97	27
03070A	0.69	4.58	30	97	
03120	1.38	8.01	24	120	
03130	1.38	8.01	15	122	25
03140	1.38	8.01	25	127	
03150	1.38	6.87	18	112	26
03180	0.34	8.01	20	114	26
03190	0.34	8.85	15	127	25
03210	0.34	7.44	18	124	

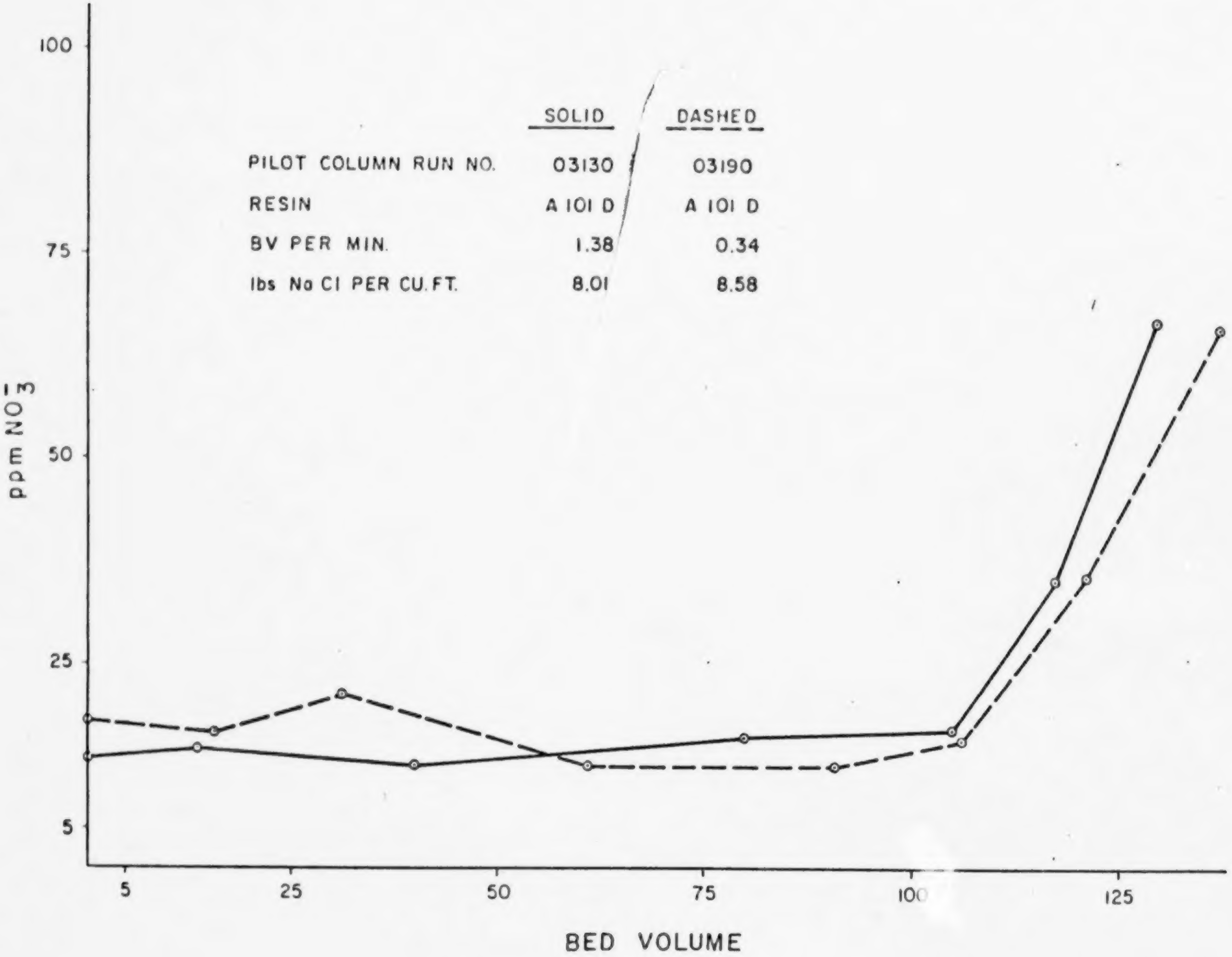

FIGURE A-25 PILOT COLUMN RUNS - EFFECT OF FLOW RATE

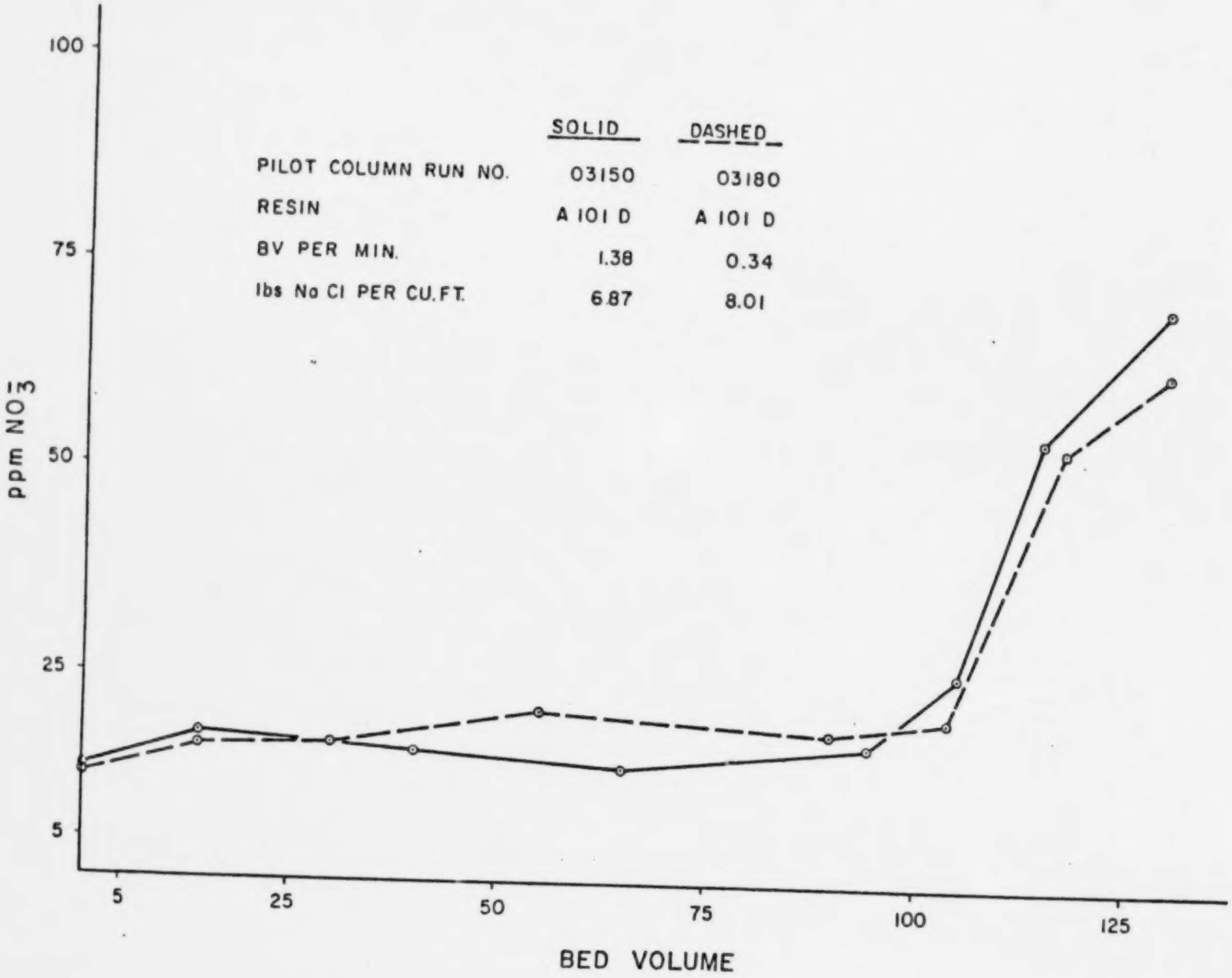

FIGURE A-26. PILOT COLUMN RUNS - EFFECT OF FLOW RATE

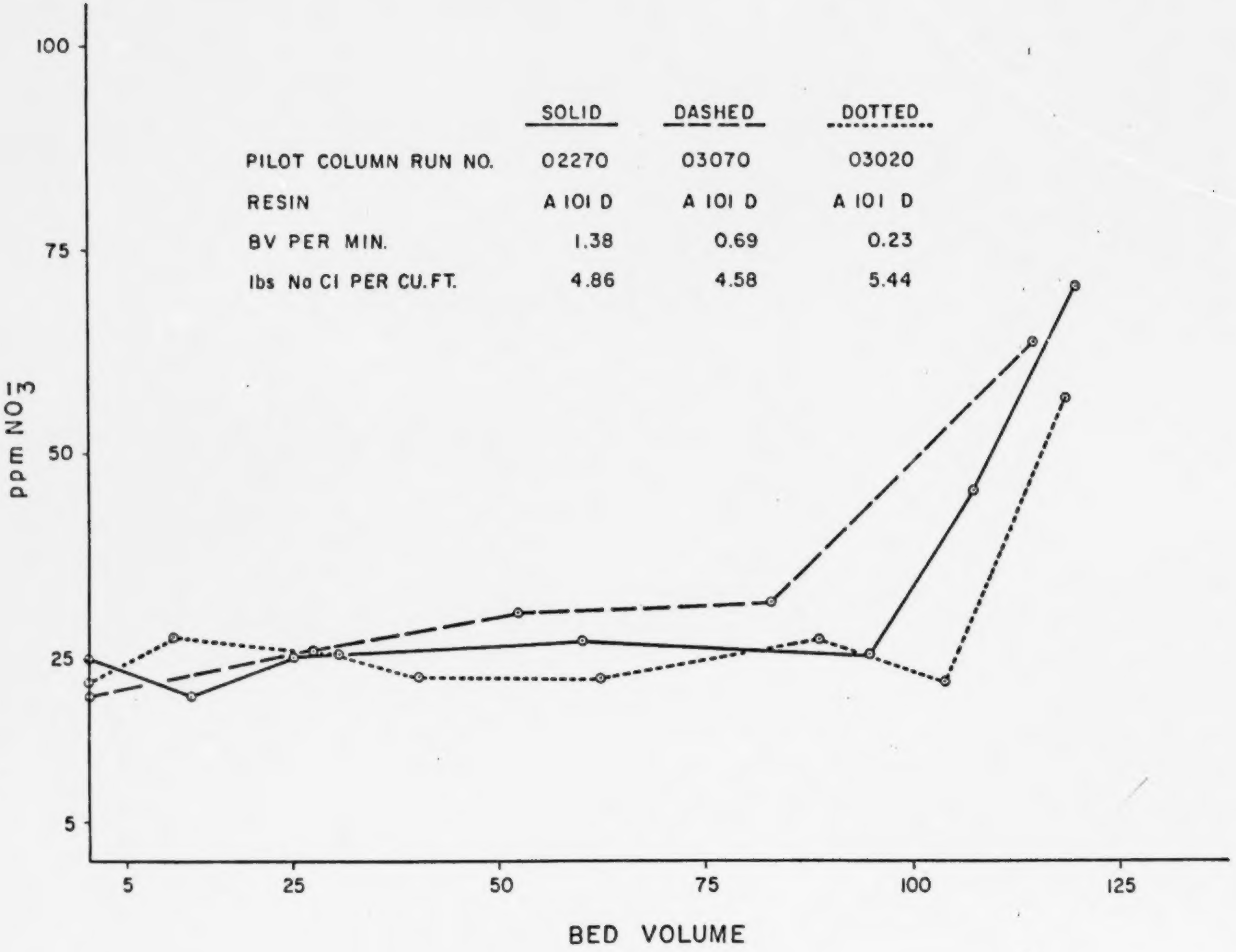

FIGURE A-27 . PILOT COLUMN RUNS - EFFECT OF FLOW RATE

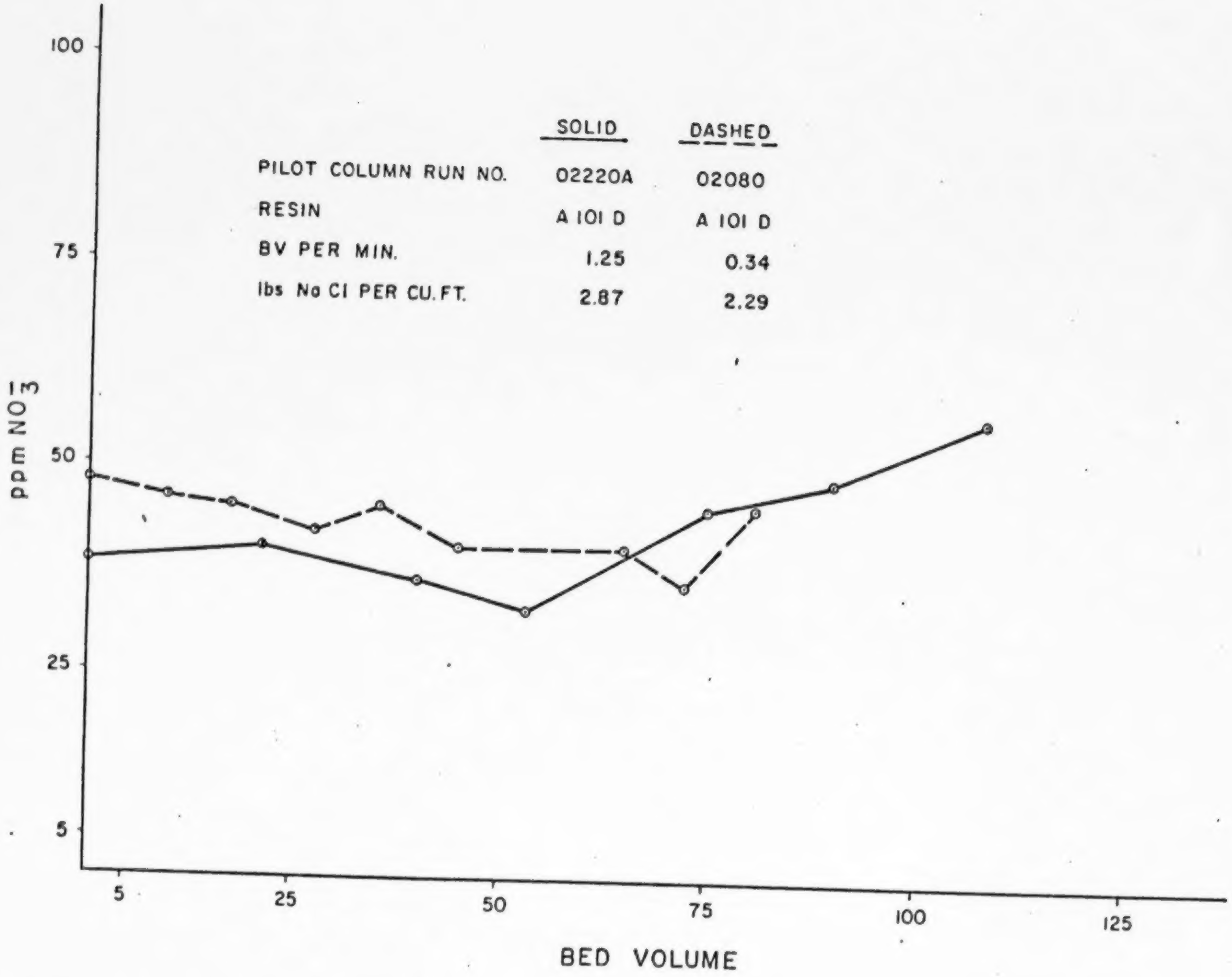

FIGURE A-28. PILOT COLUMN RUNS - EFFECT OF FLOW RATE

Residual Nitrate on Exhausted Column - Step 2

Assume that a product water of 30-ppm (0.48 meq/l) nitrate is desired. The equivalent fraction of the column remaining in the nitrate form after regeneration and at start of run is estimated from Equation (2).

$$\frac{\overline{X'_N}}{1 - \overline{X'_N}} = K_C^N \frac{X_N}{1 - X_N}$$

$$\frac{\overline{X'_N}}{1 - X'_N} = 4 \times \frac{0.039}{1 - .039} = 0.162$$

$$\overline{X'_N} = 0.139$$

Capacity of Partially Regenerated Column - Step 3

The capacity, BV(N)', of the partially regenerated column will be

$$\begin{aligned} BV(N)' &= BV(N) \times (1 - 0.139) \\ &= 150 \times .861 = 129 \end{aligned}$$

Regenerant Requirements - Step 4

Regeneration will remove all sulfate and reduce nitrate equivalent fraction on column to $X_N = 0.139$. The amount of sulfate on the column at the end of the run is

$$\begin{aligned} [\overline{SO_4}] = \underset{\text{on resin}}{\text{eq } SO_4^{=}/l} &= BV(N)' \times [SO_4^{=}] \times 10^{-3} \\ &= 129 \times 6.77 \times 10^{-3} \\ &= 0.873 \text{ eq/l} \end{aligned}$$

The equivalent fraction of nitrate, $\overline{X_N}$, on the column at the end of the run is

$$\overline{X_N} = \frac{\text{meq } NO_3^-/l \text{ on resin} \times 10^{-3}}{\text{resin capacity (eq/l)}} = \frac{[\overline{NO_3}]}{1.3}$$

$$= \frac{BV(N)'}{1.3} \times ([NO_3^-] \text{ influent} - [NO_3^-] \text{ effluent}) \times 10^{-3} + \text{equivalent fraction of column in nitrate form at start of run}$$

$$= \frac{129}{1.3} \times (1.57 - .48) \times 10^{-3} + .139$$

$$= 0.247$$

The amount of sodium chloride regenerant required to remove the sulfate is estimated on the basis of 1 eq of NaCl required for each equivalent of sulfate on the column. The amount of sodium chloride required for removal of sulfate from 1 cubic foot of resin is:

$$[\overline{SO_4}] \times 28.31 \text{ l/cu ft} = \text{eq NaCl/cu ft resin}$$

$$.873 \text{ eq/l} \times 28.31 \text{ l/cu ft} = 24.73 \text{ eq NaCl/cu ft resin}$$

$$\frac{24.73 \text{ eq NaCl/cu ft resin} \times 58.45 \text{ g/eq}}{454 \text{ g/lb}} = 3.18 \text{ lb NaCl/cu ft resin}$$

The amount of sodium chloride required to reduce $\overline{X_N}$ from 0.247 to 0.139 is estimated from Curve A of Figure A-14 as 2.24 pounds of NaCl/per cubic foot resin. The total regenerant requirement is 3.18 + 2.24 = 5.42 lb/cu ft resin.

The column will therefore treat 129 BV of Well 3 water and lower nitrate from 85 ppm to 30 ppm.

Regenerant requirements are then 5.42 pounds per (0.129 BV x 7.48) gallons = 5.62 pounds per 1,000 gallons of treated water. This can be compared to pilot column data for Well 3 shown in Figure A-21 which shows, at 5.42 pounds of NaCl per cubic foot of resin, the approximate leakage of nitrate through the column is 30 ppm. Data shown in Table A-12 (Runs 02270 through 03070A) also verifies the estimate of nitrate leakage through the column. For these runs, an average of 5.1 pounds of NaCl was used as regenerant, and the average leakage was 27.8 ppm. The BV treated by the incompletely regenerated pilot column, however, was less in each case than the estimated value of 129 BV. Bed volumes to breakthrough for all runs in Table A-12 were determined at NO_3^- = 45 ppm thus making the value lower than that obtained if this point is determined at 1/2 x (influent NO_3^- effluent NO_3^-). The average sodium chloride regenerant requirement to reduce Well 3 water to NO_3^- = 30 ppm for the above runs is 6.64 pounds per 1,000 gallons compared with the estimated 5.62 or 18 percent higher than the estimated value.

For lesser salt loadings listed in Table A-12 (Runs 01220 to 02260), the average values obtained with the pilot column compared to the estimated values are:

	Average of Runs 01220 to 02260	Estimated
NO_3^- leakage ppm	44	45
Salt loading lb/cu ft	2.40	3.76
Bed volumes treated	68.5	112
Salt loading per 1,000 gallons of Well 3 treated	4.69	4.48

For higher salt loadings listed in Table A-12 (Runs 03120 through 03210), the comparative values are:

	Average of Runs 03120 to 03210	Estimated
NO_3^- leakage ppm	22.5	22.5
Salt loading lb/cu ft	7.89	5.54
Bed volumes treated	121	134
Salt loading per 1,000 gallons Well 3 water	8.7	5.52

The discrepancy between the observed and estimated values for salt loading in this case can be attributed to the inefficiency of the regeneration process in the pilot column used coupled with the known difficulties of removing nitrate from resin where $\overline{X_N}$ is low.

ESTIMATES FOR McFARLAND WELL 2 AND OTHER WATERS

The above method is applied here to waters of other compositions to give product water of approximately 30 ppm in nitrate.

The McMWCo Well 2 has the following approximate composition:

NO_3^- = 56.7 ppm = 0.91 meq/l
HCO_3^- = 71.9 = 1.18
Cl^- = 60.5 = 1.70
$SO_4^=$ = 197 = 4.10
Total Anion = 7.89

Reduction of nitrate to 30 ppm would provide a water suitable for blending with an equal portion of raw water having a nitrate level below 60 ppm. Use of the above method to estimate the amount of regenerant to reduce nitrate at Well 2 gives the following values:

NO_3^- leakage (ppm) = 30
Salt loading (lb/cu ft) = 3.71
Bed volumes treated = 199
Salt loading per 1,000 gallons Well 2 water treated (lb) = 2.49
Salt requirement per 1,000 gallons blended water (lb) = 1.25
Cost of regenerant per 1,000 gallons of blended water @ 1.5 cents per pound = 1.88 cents

Comparative values of waters of various composition are given in Table A-13.

TABLE A-13. REGENERATION REQUIREMENTS FOR WATERS OF VARIOUS COMPOSITIONS

Water Composition → Operating Parameter ↓	NO_3^- meq/l	1	1	1.5	1.5	1.5	1.5
	HCO_3^-	1	1	1	1	1	1
	Cl^-	1	1	1	1	1	1
	$SO_4^=$	.5	3	3	2	1	.5
	Total Anion	3.5	6.0	6.5	5.5	4.5	4.0
NO_3^- in product water ppm		30	30	30	30	30	30
Bed volumes treated to breakthrough		423	229	207	247	307	347
Salt loading lb/cu ft		2.15	3.73	4.13	3.67	3.36	3.22
Salt requirement lb/1,000 gallons		0.68	2.18	2.67	1.98	1.46	1.24

The salt requirements for these waters appear remarkably low to those accustomed to thinking that ion exchange will generate large quantities of brine. These low values are made possible only by operation of an incompletely regenerated column from which nitrate can be removed by the regenerant at higher efficiency.

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